

# **ELECTROKINETIC STUDIES OF RUTILE**

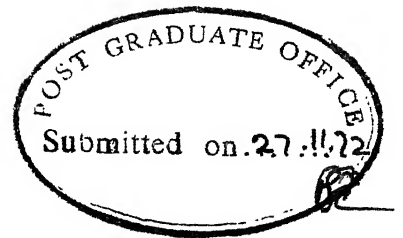
A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

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BY  
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to the

**DEPARTMENT OF METALLURGICAL ENGINEERING**  
**INDIAN INSTITUTE OF TECHNOLOGY KANPUR**  
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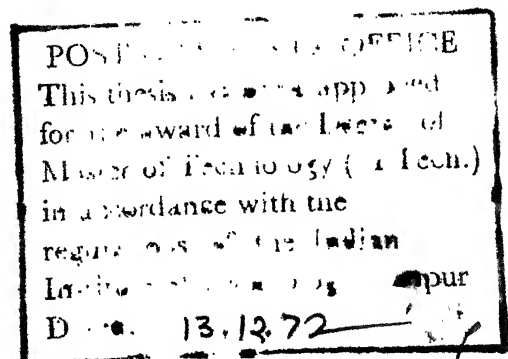


**CERTIFICATE**

**CERTIFIED THAT THE WORK "ELECTROKINETIC STUDIES OF RUTILE"  
HAS BEEN CARRIED OUT UNDER MY SUPERVISION AND SAME HAS NOT BEEN  
SUBMITTED ELSEWHERE FOR A DEGREE.**

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*AK MGS.*

( Ashok K. Misra )



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## ABSTRACT

The investigations on the electrokinetic behavior of rutile in solutions of various electrolytes and sedimentation potential of glass and rutile have been reported in this dissertation.

Sedimentation potential studies have been carried out on rutile and spherical micro-beads of glass in KCl and BaCl<sub>2</sub> solutions. To check the reliability of the results by sedimentation potential technique, corresponding studies have been made on electrophoretic mass transport analyser. The zeta potentials calculated by the two methods for same material under identical conditions seem to agree within experimental errors. A new method for finding the weight of solids between electrodes has been adopted which appears to be more reliable than that given by previous authors.

Electrokinetics of rutile (88.9% TiO<sub>2</sub>) of mineral origin has been studied in solutions of KCl, BaCl<sub>2</sub>, AlCl<sub>3</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O, sodium oleate and non-ionic surface-active agent. Based on the work done by previous workers, a new approach to the rutile-water interface has been adopted. The location of shear plane where zeta potential is measured has been suggested to be at some distance beyond the solid surface in a region of greatest disorganisation of the liquid medium. This disorganisation arises because of the opposing ordering effects on water molecules near the surface and far in the bulk. The electrokinetic results have been explained on the basis of this concept of shear plane and properties of electrolytes used.

## **1. INTRODUCTION AND LITERATURE REVIEW**

**1.1 Zeta potential :** The concept of zeta potential has revolutionised the science of colloid chemistry. Not only does it explain the behaviour of a suspension in chemical environments, but has made mathematical treatment of colloidal systems much easier. It was <sup>who observed</sup> Reuss for the first time (1808) that when a potential difference was maintained across a porous plug of wet clay or sand separating two portions of water, a flow of water occurred from one side of diaphragm to other. The observation was explained by assuming that the clay surface was charged. It has been recognized now that a solid on contact with an aqueous electrolyte solution will acquire a certain charge density localised in the plane of its surface, which will be balanced by an opposite excess charge in the liquid phase. An applied voltage will therefore cause a relative displacement of the charged layers. In other words if particles moved in aqueous medium from one position to another under the influence of some external force, a potential difference would be developed across the two positions. The electrical potential in the slipping plane between the fixed and flowing liquid is called zeta potential.

The concept of zeta potential (ZP) has been used by mineral engineers in flotation where the choice of collector often depends upon the charge on the mineral surface. Besides, zeta potential may be correlated with the coagulation property and viscosity of suspensions. Recently, interest has been shown in separating the gangue from the ore by the so called selective flocculation method<sup>D</sup>. A knowledge of zeta potential would be useful in the understanding of this method. Considerable work has been

done on the zeta potential of biological systems. Raddick<sup>2)</sup> in his interesting work has discussed the role of zeta potential in cardiovascular systems.

**1.2 Sedimentation potential :** Dorn<sup>3)</sup> discovered in 1878 that when suspended particles are forced to move through a liquid in response to gravitation, a potential gradient is generated in the direction of movement. The potential so developed is called sedimentation potential (SP). Stock<sup>4)</sup> (1913) while using organic liquids was able to harmonize his results with the familiar electrokinetic equation of Smoluchowski<sup>78)</sup>. In 1942, Quist and Nashburn<sup>5)</sup> obtained zeta potential of glass particles in water by sedimentation potential measurement. Their design of the apparatus has been used till now with slight modifications. Elton and Coworkers<sup>6,7,8,9)</sup> in a series of works on fused silica particles, attempted to calculate the zeta potential directly by measuring the sedimentation velocities of particles in aqueous systems. Because of experimental errors and mathematical approximations the approach was not pursued. Elton and Mitchell<sup>10)</sup> determined the zeta potential of carborundum in aqueous solutions by sedimentation potential method. They noted that neglect of surface conductivity could lead to serious errors. Ghosh et al<sup>11)</sup> found that sedimentation potential was independent of size of the particles as long as the particle size is much greater than the double layer thickness. Elton and Peace<sup>12)</sup> made an experimental study of sedimentation potential of glass particles in water and dilute aqueous KCl and silica, and glass particles in toluene and ether. They found sedimentation potential was independent of the size of the electrodes. They could not interpret the potentials obtained



in non-aqueous media on the basis of electrokinetic equations. The experimental technique used by them was similar to that of Quist and Washburn, except that particles were previously equilibrated with the solution by prolonged shaking. Peace and Elton<sup>13)</sup> in another series of experiments noted the sedimentation potential developed by five different solids viz. pyrex glass, fused silica, silicon, fused alumina and carborundum, in KCl and BaCl<sub>2</sub> solutions over the concentration ranges  $1-7 \times 10^{-5}M$ . They considered the effect of temperature also. In the end they emphasised the need of stating the method of preparation and cleaning the surface which affects the measured potentials. Roy<sup>14)</sup> calculated the zeta potential of quartz particles of graded size in dilute KCl solution by electro-osmotic and sedimentation potential methods. The values obtained were 124 mV and 133 mV respectively giving a satisfactory agreement. Rastogi and Misra<sup>15)</sup> measured the sedimentation potential in pyrex-water and quartz-water systems. They compared the values of zeta potential so obtained with that calculated from electrophoretic mobility. Irreversible thermodynamic theory was developed for electrophoresis and sedimentation potential. The cross-phenomenological co-efficients were evaluated and Onsager's reciprocal relationship was found to be valid<sup>15,16)</sup>. The ratio of zeta potential computed from sedimentation potential and electrophoretic mobility was 1.6 for pyrex-water and 1.65 for quartz-water systems. Since the glass particles could not be observed visually (to calculate the sedimentation velocity), they used an optical assembly by which the particle movement could be noted. In their second publication<sup>16)</sup> they gave a mathematical expression to include the effect of surface conductance in calculating the sedimentation potential. Cohen et al<sup>17)</sup> have described a method to determine the sedimentation potential of canine erythrocytes.

**1.3 Zeta potential of Rutile :** Considerable work has been done regarding the electrokinetic phenomenon of rutile and anatase. Graham and Madely<sup>18)</sup> reported the zero point of charge (ZPC) of beach sand deposits of rutile to be around a pH of 3.5. Purcell and Sun<sup>19)</sup> reported the ZPC of high purity (99.89%) synthetic rutile at pH of 6.8. The addition of NaCl ( $10^{-3}M$ ) had no effect on ZPC, while  $Na_2SO_4$  reduced it and for  $CaCl_2$  ( $10^{-3}M$ ) the surface was always positive for the pH ranges studied. They also studied the effect of sodium oleate, sodium linoleate and sodium linolenate in various concentration at different values of pH. They explained their results on the basis of adsorption and nature of surface of rutile. Huber Otto et al<sup>20)</sup> reported ZPC at a pH of 7 for high purity rutile. Kogun et al<sup>21)</sup> and Medvedev<sup>22)</sup> studied electrokinetic properties with pH as variable for rutile and anatase. Wiseman<sup>23)</sup> reported the electrophoretic mobility values of rutile pigment with pH as variable whereas Funikatsu et al<sup>24)</sup> reported the same but in presence of orthophosphates, pyrophosphates and triphosphates. Morimoto and Sakamoto<sup>25)</sup> tried to find the dependence of electrokinetic potential and surface acidity of rutile on its heat treatment to clarify the dissociation of hydroxyl groups on its surface. In other series of experiments, they<sup>26)</sup> reported the effect of electrolytes on samples calcined at different temperatures. The effect of trace water on zeta potential of rutile in organic liquids like heptanol, nitrobenzene, aerosol-OF has been studied by Zettlemoyer<sup>27)</sup>, McGown et al<sup>28,29,30)</sup> and Micale et al<sup>31)</sup>. Effect of surface active agents on the zeta potential of rutile has been studied by Makismova et al<sup>32,33,34)</sup> and Kogun et al<sup>21)</sup>. Kogun and Bexilevich<sup>35)</sup> studied the effect of varying dielectric constant by using different organic liquids on the zeta potential of rutile. Recently Berube and De Bruyn<sup>36,37)</sup> have studied the adsorption at the rutile-solution interface.

**1.4 Purpose and scope of present work :** The present work can be divided in two parts :

- 1) Sedimentation potential measurement and comparison of zeta potential computed from sedimentation potential and electrophoretic mobility measured in electrophoretic mass transport analyser (EMTA).
- 2) Zeta potential of rutile in different electrolytes.

The apparatus and method for sedimentation potential studies carried out by other authors so far has been more or less same as suggested by Quist and Washburn<sup>5)</sup> and this method involves some difficulties and errors. To achieve a reduction in these difficulties and errors some changes in the conventional method of sedimentation potential measurement were contemplated. The sedimentation potential studies have been carried out on rutile and glass. The suspending liquid in both cases has been water containing varied amounts of KCl and BaCl<sub>2</sub>. The corresponding studies have been made with EMTA and the two results compared - the purpose of comparison being to check the reliability of the sedimentation potential method. The experiments on glasspheres were carried out to study the effect of geometry of particles on the comparison.

The zeta potential studies carried out by previous authors barring a few, have been on pure and synthetic rutile.

In the present study a mineral grade of rutile (from Indian beach sand) has been studied in aqueous solutions of KCl, BaCl<sub>2</sub>, AlCl<sub>3</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O, i.e. in solutions containing cations and anions of variable valency as well as solutions containing NaOH and non-ionic surfactant. Present worker came across no reference where mineral grade was studied in all the

above electrolytes, so that some light could be thrown on natural rutile - solution interface and rational interpretations could be ascribed to the flotation behaviour of rutile - collector - moderator systems.

## 2. EXPERIMENTAL SET UP

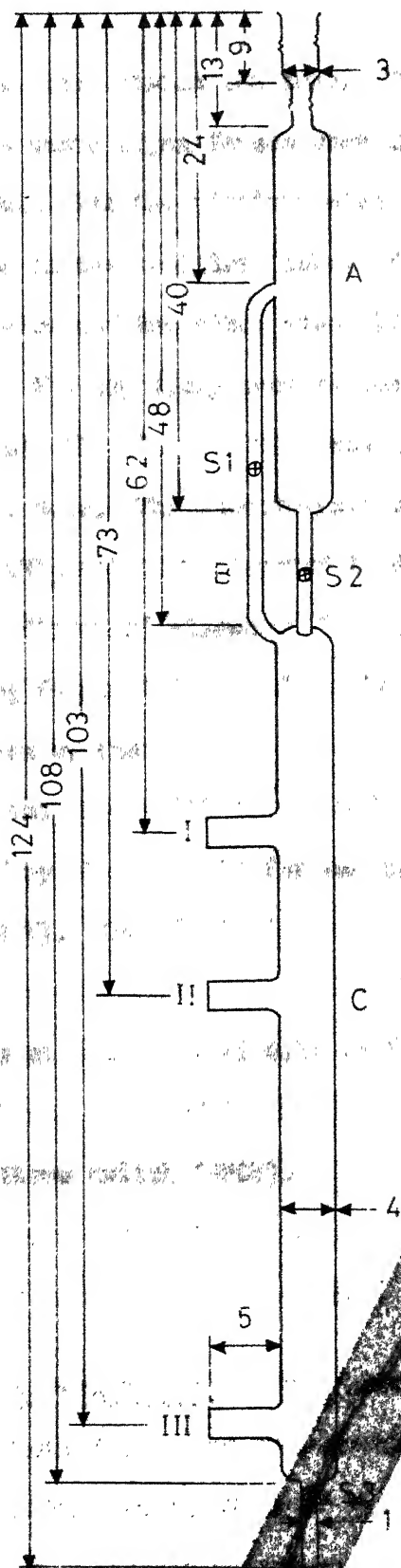
### 2.1 Sedimentation Potential :

The apparatus employed was identical to that used by Quist and Washburn<sup>5)</sup>. Its diagrammatic representation is given in figure No. 1. The apparatus consisted of a vertical tube having two parts; an upper compartment or "Holder" 'A' and a lower compartment or "Settling tube" 'C'. The two compartments were connected by a 3 mm. stop-cock 'S<sub>2</sub>' and a side arm 'B' which also had a stopcock 'S<sub>1</sub>'. The lower compartment had three ground glass joints I, II & III sealed as shown in figure 1. At the lower end of the settling tube 1 cm. dia. tube with a stopcock 'S<sub>3</sub>' was fused. The three ground glass joints served to permit insertion of the electrodes which were fixed into the inside parts of ground glass joints. The side arm 'B' was provided to permit the smooth flow of the liquid from the holder into the settling tube.

The settling tube was electrically shielded by means of a wire screen grounded to a water pipe.

The whole tube was enclosed in a wooden box which could hold the tube rigidly with ground glass joints I, II & III, protruding out of the wooden box through holes provided in the box. The wooden box had windows to permit the operation of 'S<sub>1</sub>', 'S<sub>2</sub>' & 'S<sub>3</sub>'. A steel base with four legs was designed such that it could hold the box in a vertical position.

2.1.1 Electrodes : Different types of glass electrodes used in the present study proved unsatisfactory except silver - silver chloride electrodes. The procedure adopted to prepare electrodes was more or less the same as suggested by Brown<sup>38)</sup>. Platinum wire 0.04 cm. dia. was sealed in a capillary tube leaving



Scale 1cm = 5 cm

A = HOLDER

S1 S2 & S3 = STOP COCKS  
(3 mm bore)

B = SIDE ARM

C = SETTLING CHAMBER

I II & III = B 19/24 GROUND  
GLASS JOINTS

FIG. 1 SEDIMENTATION COLUMN

about 1 cm. of wire outside the tube. The end of the wire was fused in order to remove the sharp edges formed when the wire was cut. The contact of the external circuit with the platinum wire was formed through a silver wire and a mercury column in the capillary tube. The mercury column touched on one side the platinum wire and the other side silver wire. The silver wire being fixed in position in the capillary tube through araldite adhesion. Before electrolysis was carried out, the platinum wire was checked for smooth surface and cleaned in boiling nitric acid. The electrolysis was carried out in a trough containing 0.5 - 1%  $\text{KAg}(\text{CN})_2$  solution prepared in distilled water. The preparation of silver salt has been discussed elsewhere (section 3.4). At the platinum anode,  $\text{HCN}$  was evolved and  $\text{Ag CN}$  precipitated from the solution. Contamination of the main body of the solution by the products of the anode reaction was effectively eliminated by isolating the anode with a porous diaphragm. A group of four electrodes was silver plated by electrolysis for two to three hours at a total current of 0.5 - 1.0 mA (2 - 4 V). The electrodes were then carefully rinsed and kept in distilled water. Subsequently these were chloridized by electrolysis for half an hour in a 0.1 N -  $\text{HCl}$  at a current of 0.25 mA for each electrode using a platinum cathode, the current being reversed for a short time every 4 - 5 minutes through a double pole double throw switch (DPDT). The electrodes after chloridization were rinsed in running water for twenty four hours. They were further fixed by araldite to the inside part of the ground glass joint.

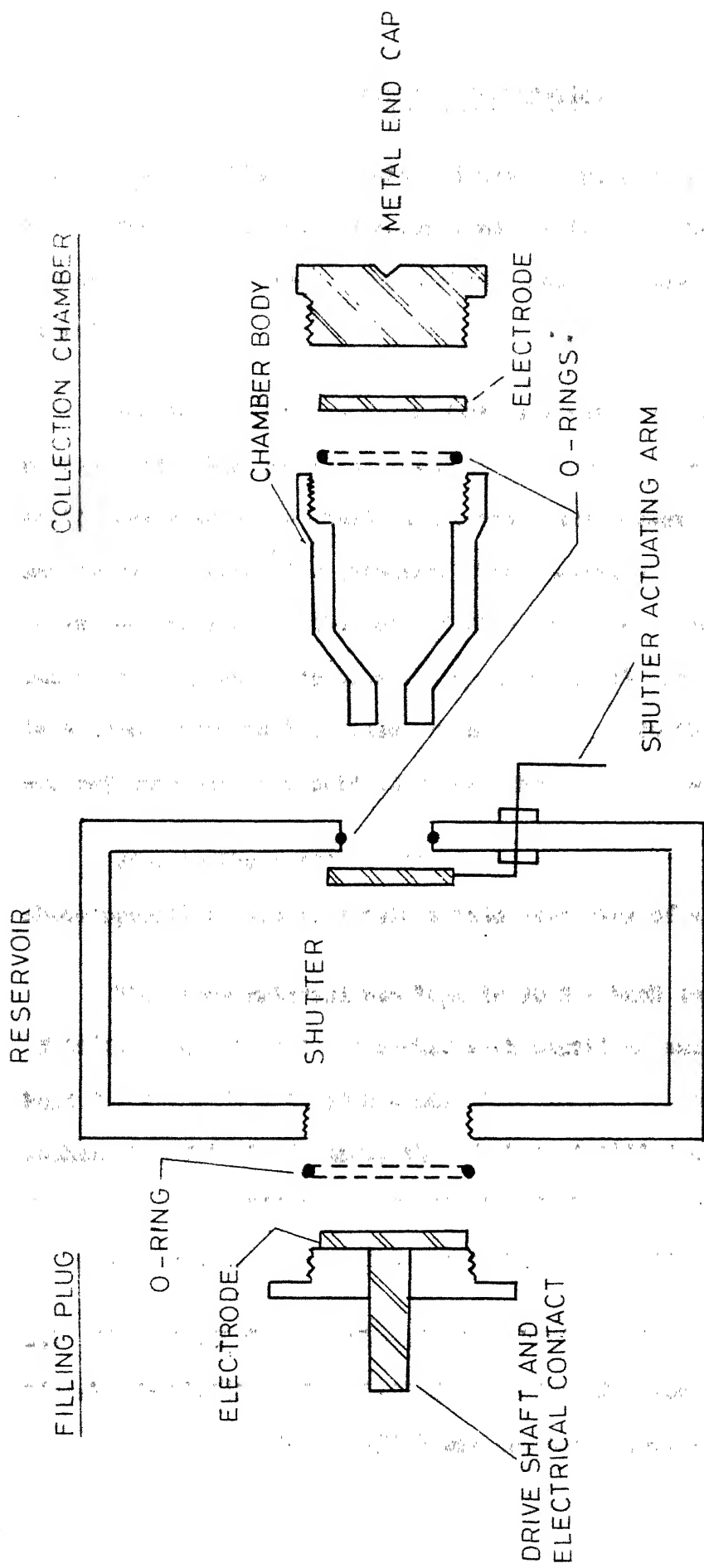
**2.1.2 Voltage Measurement :** The voltage measurements were carried out by a Vacuum tube voltmeter and micro-voltmeter. The former was a DC-Vacuum Tube Voltmeter (DC-VTM)<sup>1</sup>, model 412 A of Hewlett Packard, USA make. It could read from  $10^{-5}$  V to 300 V. Besides it had a very high internal impedance coil and less than 0.1% reading error. The micro-voltmeter was a Microvolt Indicating Amplifier<sup>2</sup>.

(Cat. No. 9835 - B) of Leeds & Northrup Co., Philadelphia, USA, make. It could read accurately any voltage between  $10^{-6}$  V to  $10^{-5}$  V and was mostly used for rechecking the 'DC-VTVM' reading at low voltage ranges. It had also a very high internal impedance coil and negligible reading error.

**2.2 Electrophoretic Mobility :** Electrophoretic mobility measurements were carried out on a Humineco model MIC - 1201 Mass Transport Analyser.

In this method the electrophoretic mobility (EM) of solid particles is determined by measuring the rate at which the particles migrate in an electric field. To this end, the whole assembly is designed to consist of a reservoir, filling plug and a collection chamber. The instrument has inbuilt wide range constant current D.C. power supply, a preset timer and motor drive for rotating the cell assembly. The cell assembly is rotated at 30 rpm. during the experiment in order to eliminate gravitational settling of coarse particles as a factor and to dissipate thermal convection currents that may be created by the current passing through the suspension. Calculations<sup>39)</sup> show that the temperature increase is never more than 1°C.





3.2. SCHEMATIC DIAGRAM OF MASS TRANSPORT CELL ASSEMBLY.

### 3. MATERIAL PREPARATION

**3.1 Rutile :** The rutile mineral used in present study was supplied by Indian Rare Earth Ltd. It was of beach sand origin (from Kerala). Washed rutile was identified under X-rays. The washed sample on chemical analysis showed 88.9% titanium dioxide.

The rutile was washed in dust free water several times and then ground in pebble mill. The ground material in the form of suspension containing 5 - 10% solids was allowed to stand in a three litre beaker for 5 minutes. The settled matter was rejected for grinding. The operation was repeated twice with the unsettled material in the form of 2% suspension. The unsettled matter from above was mixed with water to make a suspension of 1% and kept standing for 20 minutes in a three litre beaker filled with suspension to the top. The unsettled matter was rejected and with settled matter the operation was repeated twice.

Finally the settled matter was kept aside for washing. The purpose of above operations was to obtain rutile particles of sizes of very close range.

The above material was kept in 10 N - NaOH for three days at a temperature of 50°C. The material was washed with distilled water. The washed material was kept for three days in 10 N - HCl at a temperature of 50°C. The material was washed with deionized water, then double distilled water and finally triple distilled water till the conductivity of the washing water was  $2 \times 10^{-6}$  mho's. The washed material was dried under Vacuum and stored in an evacuated desiccator.

**3.2 Glass Particles :** The sized spherical glass beads were supplied by Microbeads Division, Cataphote Corporation, Jackson, Mississippi USA. The size range was 1 to 30 microns, which was further narrowed by a similar operation as

performed on rutile. The particles were washed in the same way as rutile particles. The washed material was dried and stored in an evacuated desiccator. The composition of the glass beads was not known.

**3.3 Sodium Oleate :** Sodium oleate was prepared from oleic acid. The oleic acid was obtained from the Hormel Institutes fatty acid project at University of Minnesota, U.S.A. Estimated purity was more than 99% as determined by gas-liquid and thin layer chromatography analysis.

The procedure adopted for preparation of NaOl from oleic acid was similar to that of Kajiji and Desai<sup>42</sup>). Equivalent amounts of oleic acid and analytical grade NaOH were transferred to a round bottom flask and 50 ml. of dry absolute alcohol was added (The ethyl alcohol used had been distilled, kept overnight over quicklime and re-distilled). The whole mass was refluxed over a water bath for about an hour. Subsequently, excess alcohol was removed by evaporation and the syrupy mass was poured hot in acetone which had been distilled after keeping overnight with calcium chloride. Sodium oleate thus precipitated was filtered and washed with acetone. The dried powder was stored in a cool dry place.

**3.4 Silver Salt :** The silver salt used for silver plating was  $KAg(CN)_2$ . The method of preparation was similar to that of Brown<sup>38</sup>). To a freshly prepared  $AgNO_3$  solution, filtered solution of  $NaCN$  was added to get a thick white precipitate of  $AgCN$ , which was washed in semi-darkness with double distilled water. An excess of silver cyanide was added to hot filtered solution containing 20% potassium cyanide. After stirring for about half an hour, undissolved silver cyanide was filtered off and the solution cooled. From this solution,  $KAg(CN)_2$  was recrystallised and dried under Vacuum. The silver plating solution was prepared by dissolving about 10 gms. of  $KAg(CN)_2$  in a litre of distilled water.

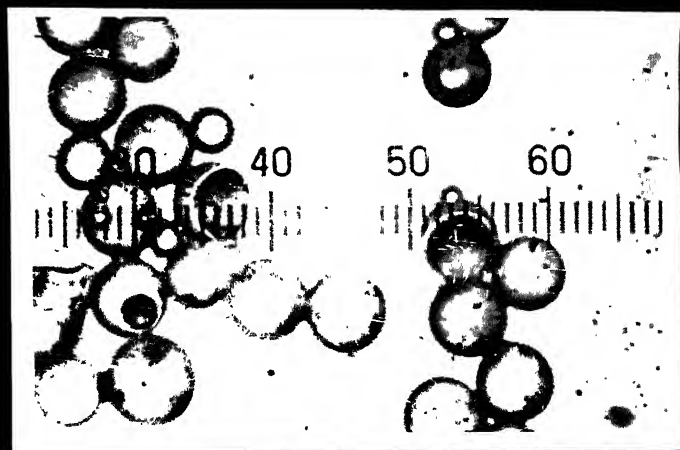
Free cyanide was reduced to a minimum by adding enough dilute  $\text{AgNO}_3$  solution to produce a faint cloud of  $\text{AgCN}$ . After this had settled, the clear solution was decanted and used for plating. A fresh solution was prepared everytime electrolysis was carried out.

**3.5 Other Chemicals :** All other chemicals used in the present study were of A.R. Grade. The non-ionic used was Tri-propylene glycol monomethyl ether - the purified chief ingredient in the commercial product. It was supplied under trade name of Dow - Froth 250 supplied by Dow Chemical Co. Michigan, U.S.A.

The water used in the present work was triple distilled, twice distilled with  $\text{KMnO}_4$  giving conductivity around  $2 - 3 \times 10^{-6}$  mho's. All calculations were checked on IBM 1620.



PRINT 1 : PHOTOGRAPH OF RUTILE PARTICLES.



PRINT 2 : PHOTOGRAPH OF GLASS PARTICLES.

#### 4. EXPERIMENTAL PROCEDURE

**4.1 Sizing Analysis :** Washed and dried sample of rutile using a standard sampling technique was taken and a very dilute suspension (0.01% solids) made. The suspension was deflocculated by the addition of Tetra Sodium Pyrophosphate and spread in a very thin layer over glass strip. The strip was dried and the particles were photographed at a magnification of  $\times 400$  using an optical microscope fitted with an optical camera. The image of the developed photographs were enlarged further 7.5 times by a photographic enlarger and printed on a photographic paper. The longest dimension and a perpendicular dimension to that were measured. The means of the two dimensions was taken and after dividing by the total magnification (3000 times), the size (equivalent diameter) was obtained. The sizes of around eleven hundred particles were measured.

With glass particles, same procedure was adopted excepting that total magnification was 2000 and only one dimension was measured since the particles were spherical.

Prints (1) and (2) are the photographs of the rutile particles and glass particles respectively.

Tables(1) and (2) under Appendix A give the size ranges of glass and rutile particles respectively. For rutile more than 80% particles fall in the size range of 2.5 and 7.5 microns. For glass more than 90% particles fall in the size range 5-15 microns.

**4.2 X-ray Analysis :** X-ray spectrometric pattern of rutile was taken with Copper as the target material. The pattern is given in figure 3. Peaks correspond

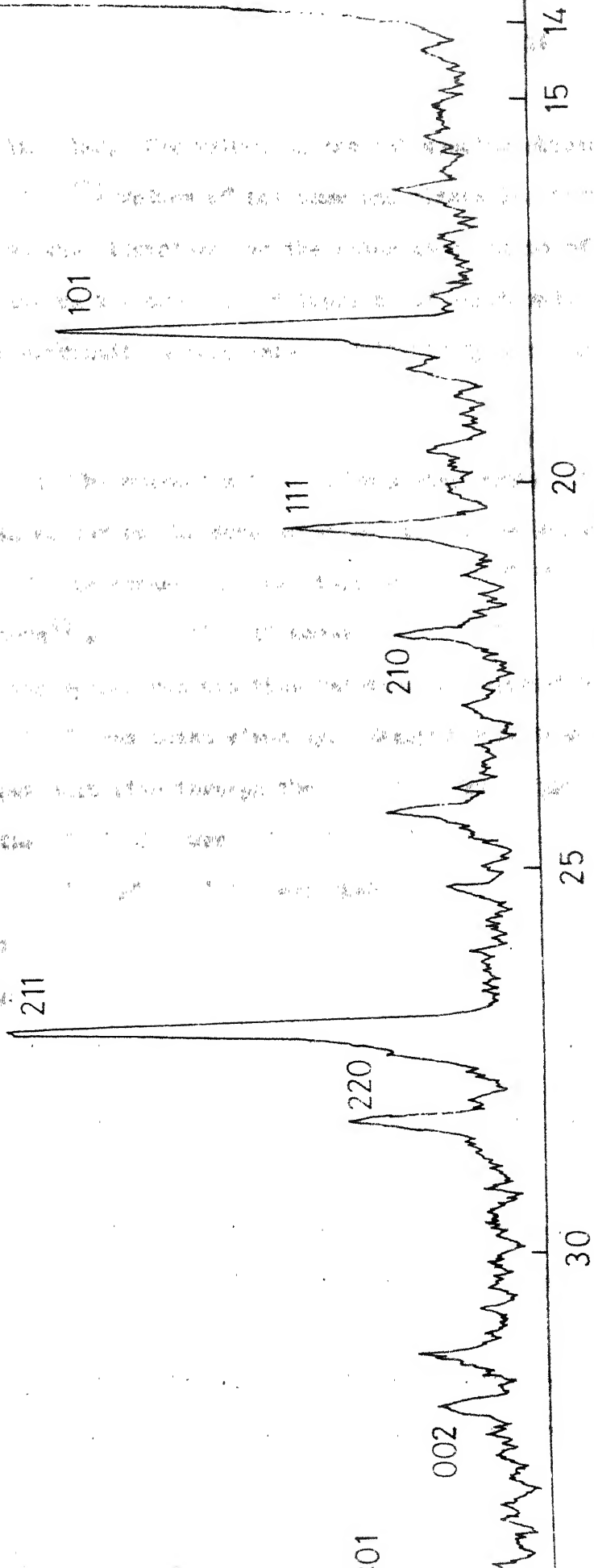


FIG. 3 X-RAY FLUORESCENT PATTERN OF RUTILE.

to various planes have been labelled. The values of the 'd' spacing obtained were compared with the literature<sup>45)</sup> values of the same and planes identified. Table 3 under appendix B gives the literature and the calculated values of 'd' spacing. The X-ray pattern showed the presence of impurity of which only anatase could be identified. It was difficult to calculate quantitatively the amount of anatase present.

**4.3 Sedimentation Potential :** The present method differs from other methods of Sedimentation Potential in so far as the determination of the weight of particles between the electrodes is concerned. In other methods<sup>5,10-15)</sup> initially described by Quist and Washburn<sup>5)</sup> a suspension of known concentration was stored in holder. The stopcock  $S_2$  was opened and the time required for particles to fall from upper to lower electrode was noted visually. Knowing this time and quantity of powder flowing per unit time through the stopcock, the weight of the material suspended between the electrodes was calculated. In the present study a suspension of known concentration of particles was shaken in the settling chamber so as to obtain a uniform suspension through out. Knowing the volume of the liquid suspended between the electrodes and concentration of the solids in the liquid, the weight of solids suspended between the electrodes was calculated.

**4.3.1 Procedure :** The Sedimentation Potential studies were carried out in following steps :

- 1) The sedimentation column was cleaned thoroughly by hot, concentrated chromic acid and then flushed by distilled water several times, so that no trace of acid was left.
- 2) All stopcocks and ground glass joints were carefully greased - care being taken while applying that at no stage in experiment, the solution comes in direct contact with grease.



3) The Ag-AgCl electrodes (previously kept for 24 hours in 1 N - NaCl) were washed with distilled <sup>water</sup> and observed directly under eye for any white shining marks which would mean the peeling off of AgCl layer. The electrode surface was further viewed under microscope at  $\times 200$ . A smooth surface without any contrast between various regions on the electrode confirmed that no part of the AgCl layer had peeled off.

The above step became necessary to avoid faulty voltages developed. The electrodes were further tested for electrical continuity by A-V-O meter.

4) The electrodes were fitted in position in two ground glass joints 'I' and 'II'.

5) The glass joint 'III' was blocked by a closed end male ground glass joint. 'S<sub>1</sub>' and 'S<sub>2</sub>' were opened and 'S<sub>3</sub>' closed.

6) A dilute suspension (less than 0.01% solids) was prepared by washing a weighed amount of rutile with two litres of triple distilled water, the washing water rejected and suspension volume increased to one litre. The suspension was shaken for about 2 - 3 hours by a magnetic stirrer and pH and conductivity noted.

7) The electrode body was kept around 10 cms. away from the centre of the main sedimentation column.

8) Next the suspension was transferred in the sedimentation column through holder. While transferring, the tube was kept inclined so that an air gap was trapped in the ground glass joint 'I' and 'II'. This air gap ensured the lack of direct contact between the suspension and the electrode surface.

9) Stopcocks 'S<sub>1</sub>' and 'S<sub>2</sub>' were closed and whole box carrying the sedimentation column was carefully taken out of the mild steel base.

10) The contents in the settling chamber were shaken gently by rotating the wooden box along its length in a vertical plane. The shaking was done for two and a half minutes. For another half a minute, the tube was kept in horizontal

position and given a semi-circular motion about an axis running through its length. While shaking, care was taken not to allow the air gap in ground glass joints to escape.

11) Without losing any time the box was brought to vertical position, the trapped air gap to allowed to escape from the ground glass joints, and box replaced in the mild steel base.

12) After 15-20 seconds the reading on VTVM or microvoltmeter were taken randomly - twenty to thirty such readings were taken within 15 - 20 seconds. The readings were averaged to get final reading for that set.

13) The suspension was taken out by opening stopcocks 'S<sub>2</sub>' and 'S<sub>3</sub>'. The pH and conductivity were noted. The electrodes were removed, the whole column washed with triple distilled water and procedure repeated with different variable

#### 4.3.2 Observation and Precautions :

1) The whole crux of the method was shaking of the suspension. Shaking had to be gentle and care was always taken that the suspension did not come in direct contact with electrodes except towards the last thirty seconds when the readings were taken. Vigorous shaking resulted in cracking of the apparatus at stopcocks, besides spoiling the electrodes.

2) The voltage fall during the time readings were taken was less than 5%. The fall was probably because initially all the big and small particles sediment, but as time elapses, only small particles descend. If the particles are of uniform size, there will probably be no fall during the time readings are taken.

3) For readings taken for a period longer than 30 seconds, the voltage fell at a high rate due to polarisation and lesser concentration of particles.

4) If the precautions in handling the electrodes were not followed strictly, the error was anything upto 100 fold.

- 5) All the electrical connections were soldered to avoid contact potential.
- 6) The error was less when dilute suspensions were used.
- 7) Temperature of the suspension was maintained constant to  $\pm 0.1^\circ\text{C}$  for each run.
- 8) The changes in conductivity by shaking was very negligible.
- 9) Reproducibility error was 2 - 5%.

**4.3.3 Calculations :** The value of zeta potential (ZP) was calculated from the sedimentation potential (SP) using the following equation :

$$\zeta = \frac{4\pi \eta \times A \times d \times E}{DR W(d - d_0) g} \times 9 \times 10^{14} \quad (1)$$

where  $E = \text{SP (Volts)}$ ,  $\zeta = \text{ZP (mV.)}$ .

$W = \text{Total weight of solids between the electrodes (gms.)}$ .

$R = \text{specific resistance of the solution (ohms-cm.)}$ .

$A = \text{area of cross-section of the settling tube (cm}^2\text{.)}$ .

$\eta = \text{viscosity of the solution (poise)}$ .

$d = \text{density of the solid (gms./cm}^3\text{)}, d_0 = \text{density of the liquid (gms./cm}^3\text{)}$ .

$D = \text{Dielectric constant of the liquid}$ .

$g = \text{Acceleration due to gravity (cm./sec}^2\text{.)}$ .

In the present experiments, mass of solids per unit volume of suspension, 'M' was known. Hence 'W' was calculated by multiplying 'M' with the volume of the liquid between the two electrodes which was fixed (134 cm<sup>3</sup>.) for the whole set of experiments (by fixing the positions of the two electrodes permanently). Area of cross section 'A' of the tube was 10.64 cm<sup>2</sup>. Since water was used as the liquid medium,\* the above expression reduced to

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\* (The effect due to presence of electrolytes in water on viscosity, dielectric constant and density being neglected).

$$\zeta = \frac{1.0816 \times 10^8 \text{ Ed}}{R M (d - d_0)} \quad (2)$$

#### 4.4 Electrophoretic Mobility :

4.4.1 Procedure : Electrophoretic nobility measurements were carried on rutile and glass beads in different aqueous solutions. The method of sample preparation has already been discussed in Chapter 3. A known weight of the material was washed with two litres of triple distilled water, washing water rejected and total volume of suspension made to 150 ml. Different solutions were added in requisite quantities. The contents of the beaker were then stirred with a magnetic stirrer encased in pyrex glass. At the end of this period, conductivity and pH measurements were done. The suspension was poured in the collection chamber and the whole assembly weighed. It was then fixed in reservior which contained rest of suspension. The whole assembly was fixed to motor which rotated it at a speed of 30 rpm. as a result of which the rutile was maintained in a state of uniform suspension during the course of the experiment. Now fixed current of 0.2 - 5 mA was applied and the mass transport in the cell under the D.C. potential so capplied, was allowed to take place for about 5 - 10 minutes. The contents of the collection chamber were weighed at the end of the experiment to find out weight gain or loss. The change in weight would be anything upto 500  $\mu$ gms.

4.4.2 Calculations : The zeta potential/<sup>was</sup>calculated from the following expression<sup>59)</sup> derived from the Smoluchowski's equation<sup>78)</sup> :

$$\zeta = \frac{4\pi\eta}{D} \frac{\Delta w \times \lambda}{1 + t + \phi(1 - \phi)(d - d_0)} \quad (3)$$

where  $\eta$  = viscosity in poise,  $D$  = dielectric constant of medium

$\Delta w$  = change in the weight of collection chamber after experiment, in gms.,

$M$  = concentration of solids in gms./cm<sup>3</sup>. of suspension,

$\lambda$  = specific conductance in mho's.

$i$  = current in amperes flowing through the suspension for  $t$  seconds.

$$\phi = M/d$$

$d$  = density of solids (gms./cm<sup>3</sup>.),  $d_0$  = density of liquid.

$\zeta$  = zeta potential in volts.

Since ' $M$ ' was usually much less than 1 ( $< 0.08$ ), therefore ' $\phi$ ' would be still lesser hence  $(1 - \phi)$  can be taken as 1. Also since water was used as the medium in all experiments, the above expression reduces to

$$\zeta = \frac{15 \times 10^4 \times \Delta w \times \lambda \times d}{i \times t \times M (d - d_0)} \quad (4)$$

where  $\zeta$  is now in millivolts.

In the above expression we see the term ' $M$ ' which is as mentioned earlier concentration of solids in suspension expressed as gms/cm<sup>3</sup>. For one set of readings with a particular electrolyte, same suspension was used and gradually the concentration of electrolyte increased. But for each set of readings the concentration of solids ( $M$ ) could not be maintained constant, as some suspension was always lost during transferring the suspension to the reservoir. Hence a simple method of knowing the ' $M$ ' was devised for each reading. The weight ( $W_1$ ) of the completely dry collection chamber was found. The volume ( $V$ ) of collection chamber was found by weighing the chamber filled completely by water whose density at that temperature was known. For each reading weight ( $W$ ) of the chamber filled with suspension was known. From this data density of suspension could be known and by simple mass balance, the concentration ' $M$ ' in gms./cm<sup>3</sup>. was found by following equation :

$$(M + d_s) = \left(\frac{M}{d_s} + 1\right) d_s \quad (5)$$

$$d_s = \frac{M - M_1}{V}$$

where  $d_s$  = density of suspension.

From equation (5), 'M' could be found out.

**4.5 Assumptions :** The assumptions involved in derivation of equations (1) to (4) are :

- 1) The particles are non-conducting and for these, radius of curvature at any point is large as compared to the extension of double layer.
- 2) The liquid surrounding the particle has an electrical conductance, dielectric constant and viscosity equal to that in bulk phase.
- 3) There is no effect due to surface conductance of the particles.
- 4) There is no effect due to relaxation in case of electrophoresis.
- 5) In electrophoresis there is no effect of electrophoretic mobility due to rotation of the cell.

The effects due to (i) relative magnitude of the electrical double layer thickness with respect to the particle diameter, (ii) relaxation and (iii) surface conductance, are serious enough to be considered in detail.

**4.5.1 Effect due to electric double layer thickness :** Smoluchowski<sup>78)</sup> proved that the electrophoretic mobility ( $\mu_0$ ) is given by the expression

$$\mu_0 = \frac{\zeta D}{4\pi\eta} \quad \text{where } \zeta = \text{Zeta potential, } D = \text{Dielectric constant}$$

$\eta = \text{Viscosity.}$

and Hückel<sup>84)</sup> obtained  $\mu_0 = \frac{\zeta D}{6\pi\eta}$ .

The discrepancy in the two above equations is due to difference in the concept regarding geometry of applied field. Henry<sup>85,86</sup> showed that

$$u_s = \frac{\zeta D}{4\pi\eta} f(\kappa a)$$

where

$$\kappa^2 = \frac{4\pi e^2 \sum n_i Z_i^2}{D K T}$$

$a$  = radius of the particle (cm.),  $e$  = electronic charge in e.s.u.

$n_i$  = number of 'i' ions/cm<sup>3</sup>. in bulk.

$Z_i$  = valency of 'i' ions.

$K$  = Boltzmann's constant (erg/k°/ion)

$D$  = Dielectric constant,  $T$  = Temperature (k°).

$f(\kappa a)$  for low values (' $\kappa a$ ' less than 0.1) is 2/3, thus resulting in Hückel's equation. For ' $\kappa a$ ' greater than 100 the correction factor to Smoluchowski equation is unity. The precise values of  $f(\kappa a)$  for  $\kappa a = 0.1$  to 100 are given in Henry's paper and should be consulted unless ' $\kappa a$ ' is larger than 100 or when  $a \gg 1/\kappa$ , the electrical double layer thickness.

**4.5.2 Relaxation effect :** This effect originates because of the deformation of double layer. When an electrical field is applied as in EMFA, the charge of the double layer is displaced in a direction opposite to the movement of the particle. Not only does this charge retard the electrophoresis by its movement, but also by the dissymmetry of the double layer resulting from this displacement, a retarding potential difference is set up<sup>87</sup>). The correction factor because of relaxation effect can be obtained for electrolytes of different valencies in terms of ' $\kappa a$ ', from Henry's paper.



In Krut's<sup>79)</sup> book functions  $f(\kappa a)$  for different electrolytes have been plotted indicating the compound effect due to factors mentioned in Sections (4.2.1) and (4.2.2). Though in this graph correction factors for Hückel's equation have been plotted, but by changing the scale of correction factor from 0 - 1.5 to 0 - 1.0, the values can be used for the Smoluchowski's equation which has been used in the derivation of equation (3). In appendix 'F' the values of ' $\kappa a$ ' have been calculated for rutile and glass in KCl (Table 15) and BaCl<sub>2</sub> (Table 16). From the plot in Krut's book, one can see that for these values of ' $\kappa a$ ' the correction factors range from 0.95 to 1.0, except at a concentration of  $10^{-6}M$  for both KCl and BaCl<sub>2</sub>. The correction factor at these values of concentration is around 0.90. In absence of correction factor due to thickness of double layer in case of sedimentation potential, the correction factor for electrophoretic mobility at  $10^{-6}M$  KCl and BaCl<sub>2</sub> has not <sup>been</sup> considered to avoid errors in comparison (In figures '5' and '6', the values of zeta potential have been shown as tentative values at these concentration). Neglect of this correction factor at this concentration in both cases, however does not alter the trend in the zeta potential curves and hence discussion except that the absolute values of zeta potential at this concentration factor would be higher by about 10%. At concentrations other than  $10^{-6}M$  of KCl and BaCl<sub>2</sub>, the correction factor being above 0.95, has been neglected. For AlCl<sub>3</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O, the factor ' $\kappa a$ ' will be even higher because of larger valencies of the ions. Hence in these cases too, the effects due to electrical double layer thickness and relaxation can be neglected. In NaCl and non-ionic NaCl, lack of complete data (Degree of Ionization for NaCl), prevents the incorporation of correction factor in calculating the zeta potential.



**4.5.3 Surface conductivity effect :** The correction necessary for this effect has been suggested by many workers<sup>14,16,40</sup>) etc. All these corrections include the surface conductivity of particles. Howe and Pope<sup>82</sup>) have plotted the surface conductivity values of rutile against the relative humidity in the atmosphere around the experimental sample of rutile. However these values of surface conductivity are not of much use under the present experimental conditions, since it is difficult to know which value of surface conductance to select. No other reference regarding surface conductivity of rutile seems to be available in the literature. One may attempt to obtain the approximate effect due to surface conductance. For simplicity, we will select the correction suggested by Rastogi and Misra<sup>16</sup>). They have replaced the conductivity ( $K$ ) of the solution by  $K + 2 K_s/R$  to include the effect of surface conductivity where  $K_s$  is surface conductance of particles and  $R$  is the radius of the sedimenting tube. The minimum value of  $K$  in the present study has been  $2 \times 10^{-6}$  mho's. The value of  $R$  is 1.84 cms. If the value of  $K_s$  is  $10^{-8}$  mho's or below the effect due to surface conductivity can be ignored. From the paper of Howe and Pope it appears that 100% relative humidity would probably correspond to the condition of rutile in water. At this point the surface conductivity of rutile under all conditions of pre-treatment is around  $10^{-8}$  mho's and hence from the above reasoning the effect due to surface conductivity can probably have no effect. In case of glass spheres the values of surface conductance would be around  $10^{-9}$  mho's<sup>80</sup>) hence here also effect due to surface conduction need not be considered. In case of electrophoresis the basic condition<sup>81</sup>) for neglecting the surface conductivity is

$$K_s \ll K a$$

where  $K_s$  and  $K$  are conductivities of surface and solution respectively,  $a$  is one of the main dimensions of the particles. For glass the effect can neglected

but for rutile especially at low concentration of electrolyte the effect could be significant, but in absence of reliable data of surface conductivity of rutile in the present experimental conditions, it is not possible to apply the correction.

## 5. RESULTS AND DISCUSSION

**5.1 Sedimentation potential :** Discussion of the sedimentation potential experiments and results has been carried out in two parts. First part deals with the comparison of the methods suggested by author and Quist and Washburn<sup>5</sup>). The second part deals with the comparison of zeta potential values obtained by sedimentation potential ( $\zeta_{sp}$ ) measurements and electrophoretic mobility ( $\zeta_{em}$ ) measurements.

**5.1.1 Comparison of the two methods :** The difficulties and errors involved in calculating zeta potential by the method suggested by Quist and Washburn and adopted by others are :

1) Their method of calculating the quantity of power flowing per unit time through the stopcock 'S<sub>2</sub>' can give rise to errors on account of following reasons :

i) It is difficult to maintain a uniform suspension in the holder, since suspension remains in holder for a time large enough to permit the settling of particles.

ii) The mathematical equations used in derivation assume a uniform flow through the stopcock 'S<sub>2</sub>'. Since the flow will depend upon the hydrostatic pressure head in the holder, which keeps on decreasing as the suspension flows in sedimentation tube, there cannot be a uniform flow.

2) Some time air bubble is trapped in the stopper and escapes one's notice. This air bubble besides giving faulty flow rates, causes intermittence in the flow of suspension.

3) There are several experimental steps like determination of rate of settling of particles, opening of stopper for fixed interval etc. which involve human

errors of variable magnitude.

The method employed by author takes care of the above errors and difficulties, but involves the following limitations :

- 1) The free settling could be affected by shaking. However this was minimised by shaking it gently and letting the suspension to come to equilibrium for about 15 seconds after shaking. A more or less uniform voltage was developed, and this indicated that free settling conditions had been attained.
- 2) The electrodes got damaged more frequently.
- 3) The present method is time consuming and needs more experience to handle.
- 4) The solid particles come in contact with the electrodes during actual measurement which can give faulty voltages. However this can be eliminated by an improved design.
- 5) Because of the above difficulty, the particles especially small ones could get embedded in AgCl layer of electrode. It was difficult in case of rutile to identify these particles because of absence of good contrast under microscope.

Since it is difficult to make a quantitative assessment of the errors in the two methods, it becomes difficult to suggest which method is better. However some light can be thrown on their reliability if for a particular sample, zeta potential is calculated by both method under identical conditions and these are compared to zeta potential values determined for the same sample and under similar condition by a different but more reliable method. For this purpose, zeta potential was calculated for rutile in triple distilled water from sedimentation potential measurements employing the method of Quist and Washburn and that of author. Further, these values had been compared with the zeta potential calculated from electrophoretic mobility measurements in 'EMTA' technique.

The values obtained are given below : \*

Method	EM measurement	SP method of Author	SP method of Quist and Washburn
Zeta potential	-24.39 (mV)	-22.98 (mV)	-37.92 (mV)

From this data it appears that under the present conditions of experiment, the method suggested by author is reliable.

**5.1.2 Comparison of  $\zeta_{sp}$  and  $\zeta_{em}$  :** The zeta potential of rutile and glass spheres calculated from the 'SP' method has been compared with the zeta potential obtained by the 'EMTA' technique.

**Rutile :** Studies of rutile has been made in KCl and BaCl<sub>2</sub> solution by 'SP' technique and compared with corresponding measurements by 'EMTA' method. Under appendix C, table 4 gives the values of  $\zeta_{sp}$  and table 6 gives the values of  $\zeta_{em}$ . Figure 5 gives the curves for ' $\zeta_{em}$ ' and ' $\zeta_{sp}$ ' for rutile in KCl solution. The comparison is not very good especially in the concentration ranges of  $10^{-5}$  M and  $8 \times 10^{-5}$  M. The precise reason for this is not known but could be due to one or more of the errors listed in section 5.1.1.

Figure 6 gives the zeta potential curves of rutile calculated by 'SP' method and 'EMTA' technique in aqueous solutions containing BaCl<sub>2</sub>. The comparison is excellent except at a concentration of  $10^{-5}$  M of BaCl<sub>2</sub>.

**Glass :** Table 5 (appendix 'C') and Table 7 (appendix 'D') list the values of ' $\zeta_{sp}$ ' and ' $\zeta_{em}$ ' of glass in KCl and BaCl<sub>2</sub>. On comparing these values obtained by

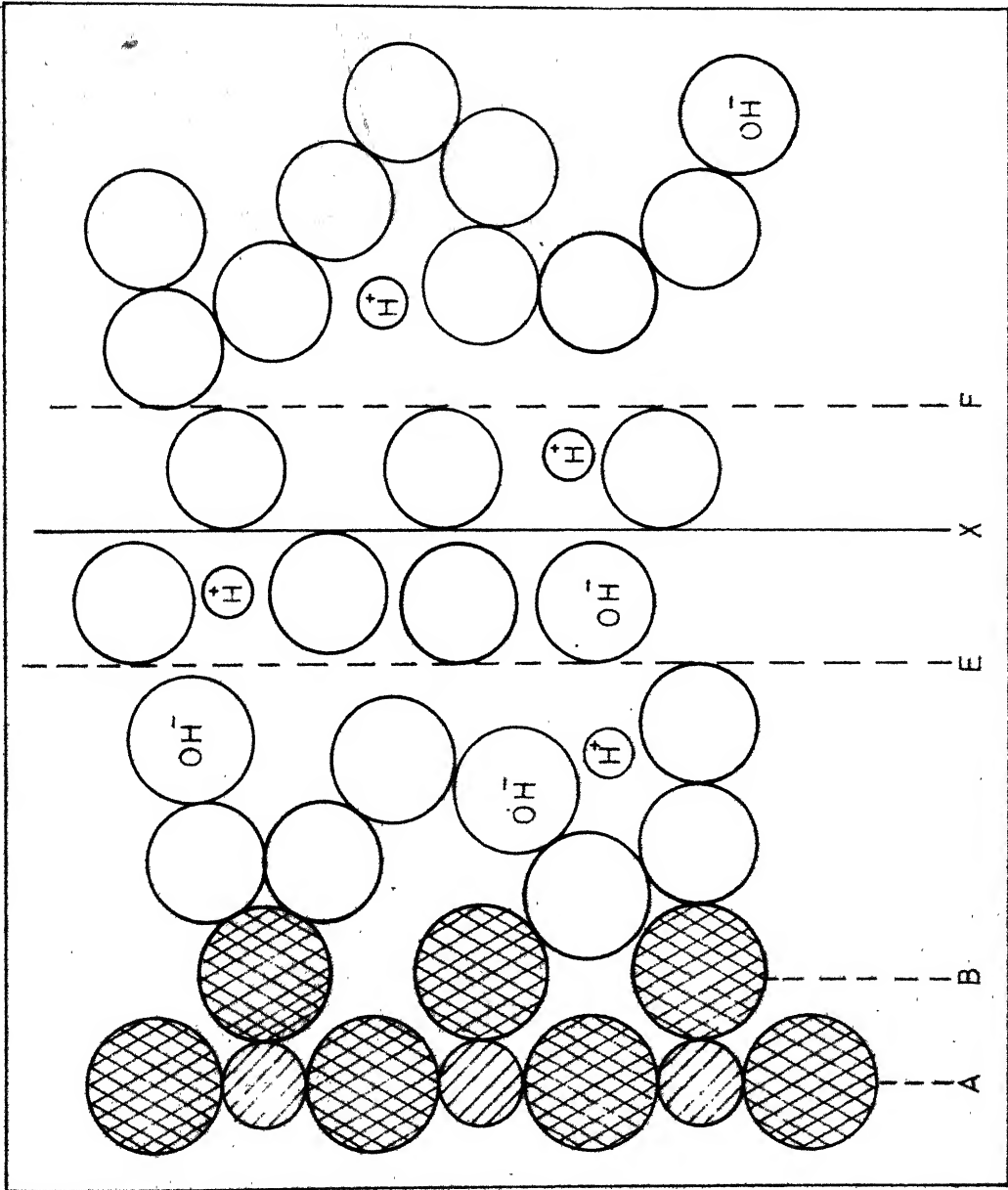
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\* The details of the calculations are given in Appendix G. The reproducibility error for the method of Quist and Washburn was 4 - 5%.

other workers<sup>12,14,16</sup> etc.), the present values look very less in magnitude and change in zeta potential with concentration of KCl is very significant, whereas with these workers the change is insignificant especially in concentration ranges of  $10^{-5}$  -  $10^{-6}$  M. The possible reason for this may be that the composition of glass beads used in present work is different from the composition of glass beads used by others. Figures 7 and 8 give the ' $\zeta_{en}$ ' and ' $\zeta_{sp}$ ' curves in KCl and  $BaCl_2$  respectively. The comparison looks reasonably good but the values of zeta potential are a bit more negative for sedimentation potential than electrophoretic mobility methods. No precise reason is known.

Another way of comparing ' $\zeta_{sp}$ ' and ' $\zeta_{en}$ ' is to take ratio of these values for the same sample under identical conditions. The values of the ratio of ' $\zeta_{en}$ ' to ' $\zeta_{sp}$ ' have been listed in appendix 'B'. Table 13 and 14 give the values of the ratio in KCl and  $BaCl_2$  solutions for rutile and glass. In case of rutile in KCl the ratio varies from 0.62 to 1.06. For  $BaCl_2$  solution except at a concentration of  $10^{-5}$  M, the ratio varies from 1.01 to 1.20. In case of glass the ratios are far from unity as electrolyte concentration is increased. At high concentration of electrolyte the ratios are very small, but that may be because the absolute values of zeta potential are very low. The ratios from Rastogi and Misra's<sup>16</sup>) data are 1.6, 1.65, 1.85 for pyrex + water, quartz + water and pyrex + acetone systems. Ratios calculated from the authors data on rutile are nearer to unity than those of Rastogi and Misra. For spherical glass beads also in some cases the ratios are nearer to unity.

Overbeck has commented<sup>79</sup>) on the comparability of the zeta potential values for the same system obtained by (i) Streaming potential (ii) Electro-osmosis and (iii) electrophoretic mobility measurements. Literature on zeta



$Ti^{4+}$

Surface hydroxyl groups.

Water molecules

A= Rutile surface

B= Hydroxylated surface layer.

X= Shear plane

BE= Region of ordered water molecules

EF= Region of high structural disorder.

FIG.4 SCHEMATIC PICTURE OF INTERFACIAL REGION SEPARATING RUTILE SURFACE FROM THE BULK LIQUID PHASE. (According to Berube + Debruyne<sup>37</sup>)

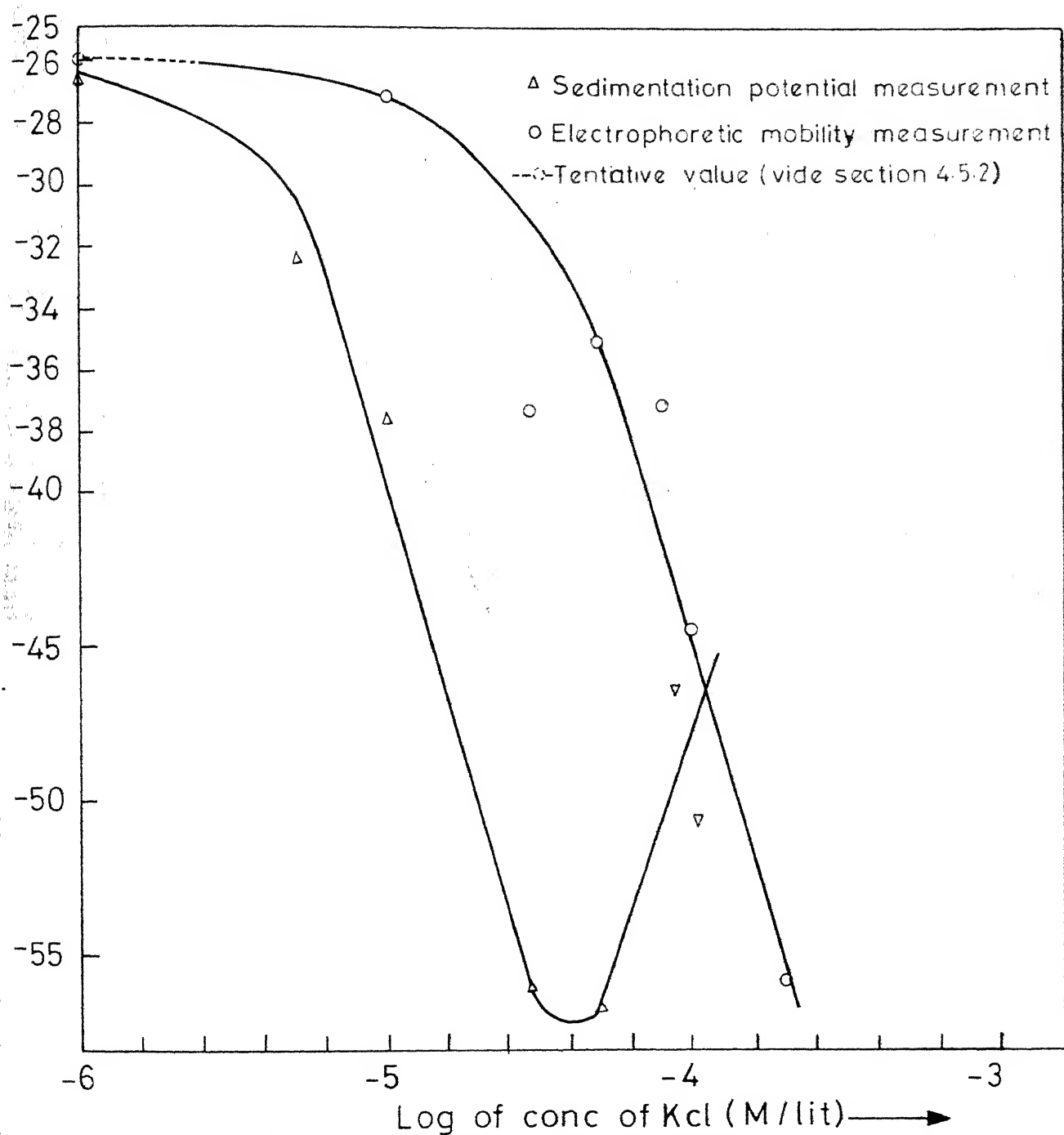


FIG. 5 COMPARISON OF ZETA POTENTIAL OF RUTILE BY  
 SEDIMENTATION POTENTIAL & ELECTROPHORETIC  
 MOBILITY MEASUREMENT IN POTASSIUM CHLORIDE  
 SOLUTION.



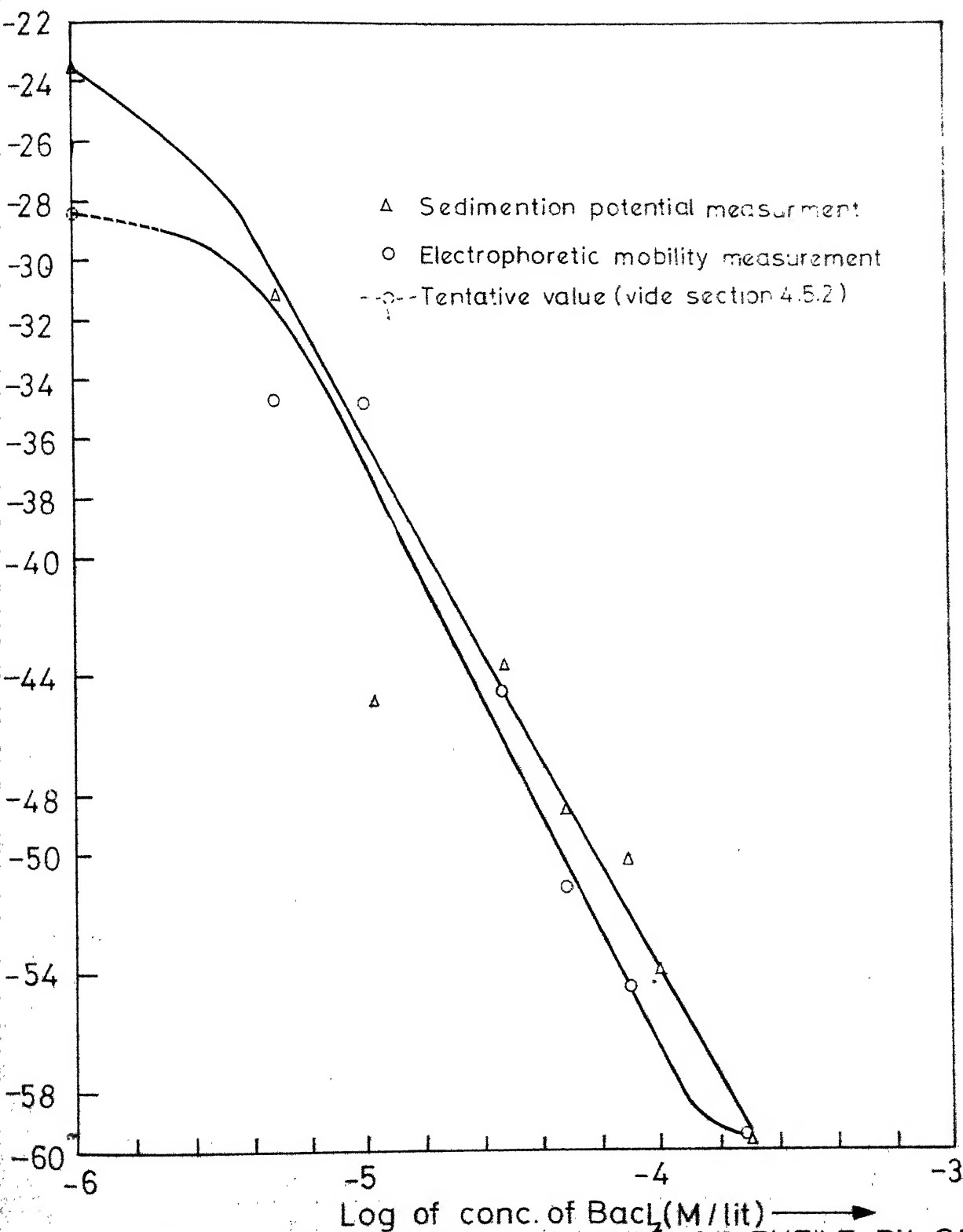


FIG. 6 COMPARISON OF ZETA POTENTIAL OF RUTILE BY SEDIMENTATION POTENTIAL & ELECTROPHORETIC MOBILITY MEASUREMENT IN BARIUMCHLORIDE SOLUTION.

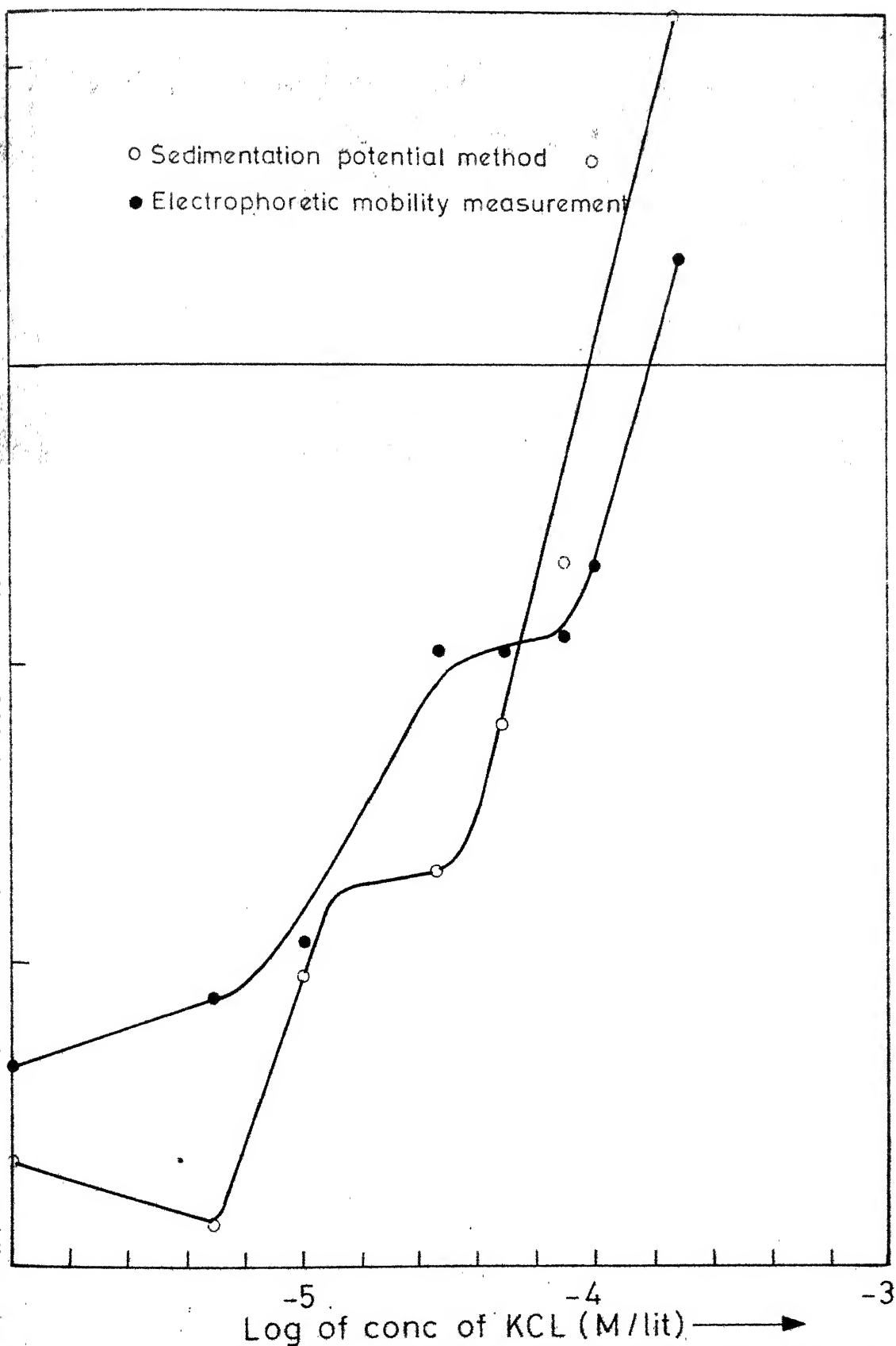


FIG. 7 COMPARISON OF ZETA-POTENTIAL OF GLASS BEADS BY SEDIMENTATION POTENTIAL & ELECTROPHORETIC MOBILITY MEASUREMENT IN POTTASIU CHLORIDE SOLUTION

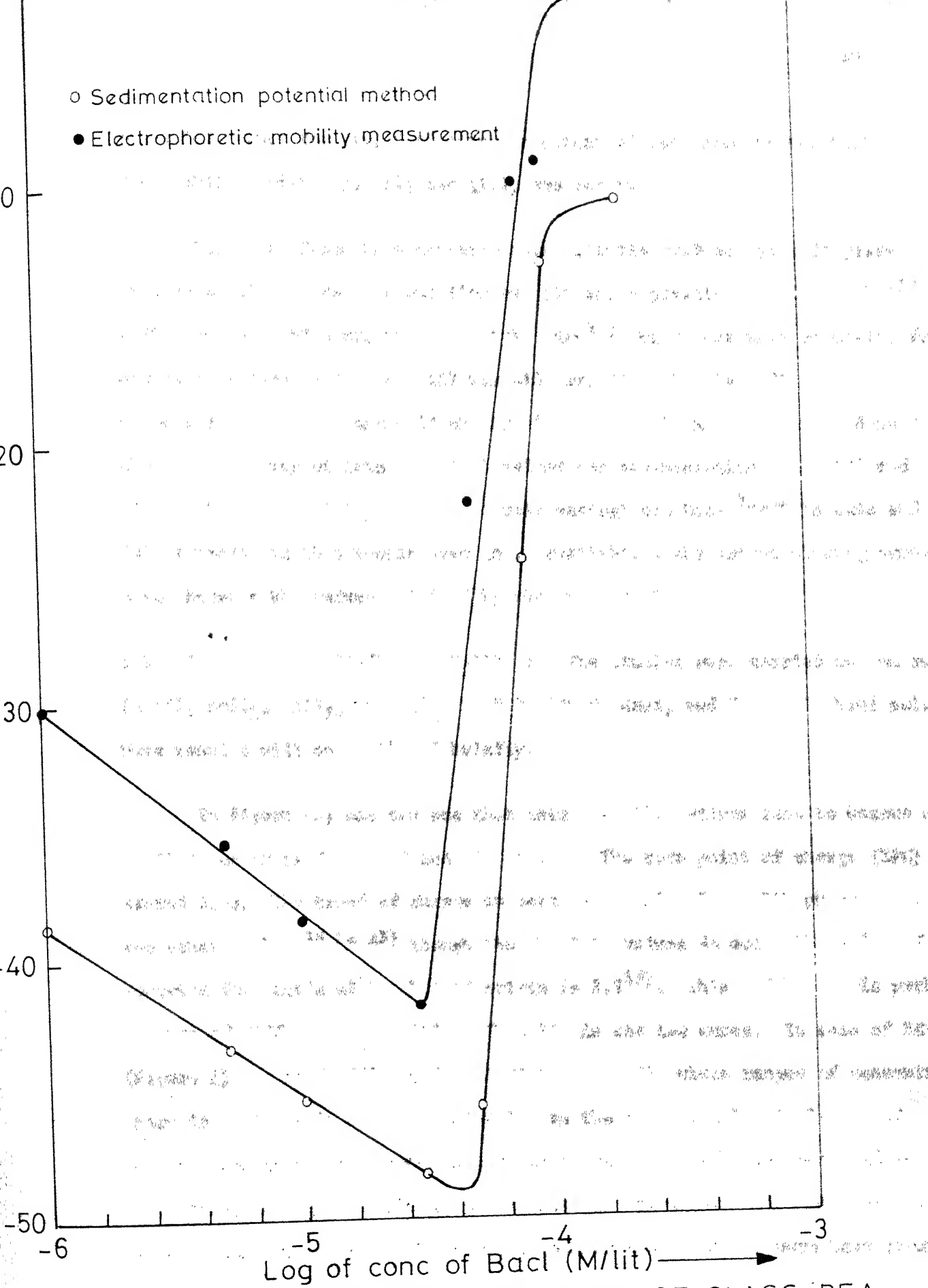


FIG.8. COMPARISON OF ZETA POTENTIAL OF GLASS BEADS BY SEDIMENTATION POTENTIAL & ELECTROPHOR-

potential values for (iv) Sedimentation potential measurements and their comparability with (i), (ii) and (iii) are scanty.

Hilton and Peace have compared zeta potential values for soft glass spheres obtained from sedimentation and streaming potential measurements<sup>13)</sup> (-76.3 mV. and -87.3 mV. respectively). Roy<sup>14)</sup> found that zeta potential for quartz particles in  $10^{-5}$  M - KCl was -133 mV. according to sedimentation potential measurement and -124 mV. by electro-osmosis measurements. Regarding the comparability of zeta potential values for sedimentation potential and electrophoretic mobility techniques only Rastogi and Misra<sup>15,16)</sup>'s data and the data reported in this thesis seem to be available - the latter showing superior match between the values obtained by the two techniques.

**5.2 Electrokinetic Studies of Rutile :** The studies were carried out on rutile in KCl, BaCl<sub>2</sub>, AlCl<sub>3</sub>, Ir(NO<sub>3</sub>)<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O, NaOH, and Non-ionic NaOH solutions. Here results will be mentioned briefly.

In Figure (9) one can see that zeta potential values tend to become more positive as pH is decreased and vice-versa. The zero point of charge (ZPC) is around 5.23. The trend of change in zeta potential values with pH agrees with the other workers<sup>18 to 23)</sup> though the absolute values do not. The value of ZPC reported for rutile of beach sand origin is 5.5<sup>18)</sup>. This difference is probably because of different composition of rutile in the two cases. In case of KCl (Figure 5) and BaCl<sub>2</sub> (Figure 6) solutions, over the whole ranges of concentrations, there is increase in negative potential as the concentration is increased. Morimoto and Sakamoto<sup>25)</sup> have also studied the change of zeta potential values with change in KCl and BaCl<sub>2</sub> concentration in solution. But their results cannot be compared with the author's results, because their samples were heat treated.

Furthermore the concentration ranges tested were high i.e. above  $10^{-4}$  M/lit. . Figures (11) and (12) show the variation of zeta potential with the change in concentration of  $\text{AlCl}_3$  and  $\text{Zr}(\text{NO}_3)_4$  in solution. In both cases after initial increase in negative potential of rutile, the negative potential tends to decrease as concentration is further increased. In case of  $\text{Zr}(\text{NO}_3)_4$ , the value at higher concentration, becomes even positive. Author came across no such reference where zeta potential of rutile had been studied in  $\text{AlCl}_3$  and  $\text{Zr}(\text{NO}_3)_4$  solutions. Figure 13 shows that with the increase in concentration of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in solution, the zeta potential increased to more negative values. Fumikatsu<sup>24)</sup> has worked on rutile in presence of this phosphate. However, the minimum concentration of electrolyte he has used is higher than the highest concentration used in the present work. Figure 14 gives the zeta potential curves in presence of Naol and non-ionic Naol. Purcell and Sun<sup>19)</sup> have worked on rutile in Naol solutions. Their values at pH 7 for Naol concentration of  $10^{-6}$ ,  $10^{-5}$ ,  $10^{-4}$  M are -15, -30, -80 millivolts respectively. On comparison with the present data in Table 11 under appendix 'D', we see their values are less negative at concentration of  $10^{-6}$  M and their zeta potential values increase at a faster rate than the author's values. Most probably this is due to the different compositions of rutile sample; their sample having more than 99.0% rutile.

The table below shows the change in zeta potential ( $\Delta ZP$ ) with increase in electrolyte concentrations from  $10^{-5}$  to  $10^{-4}$  M/lit.

Electrolyte	$\Delta ZP$	
	Rutile	Glass
KCl	-17.2	+ 18.1
$\text{BaCl}_2$	-21.8	+ 29.8
$\text{AlCl}_3$	+39.0	--

$\text{Zr}(\text{NO}_3)_4$	+ 60.0	--
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	- 14.4	--
$\text{NaCl}$	- 66.2	--

With increase in valency, both cations as well as anions seem to be more strongly adsorbed on the rutile (vide also reference 19 and 24). At lower electrolyte concentrations, anions seem to be preferentially adsorbed on rutile for all the three chlorides tested. This is true of  $\text{BaCl}_2$  and glass system as well. The role of the nature of the solid surface is also important. For example, with regard to  $\text{KCl}$  and  $\text{BaCl}_2$  solution, anions have more affinity on negatively charged rutile surface and cations on glass surface. Gaudin and Puerstmann<sup>91)</sup> have reported that quartz has more affinity for anions as the concentration of electrolyte ( $\text{NaCl}$ ) is gradually increased till about  $10^{-4}$  equ./lit. For glass surface<sup>92)</sup> and alumina<sup>93)</sup> there is charge reversal with increase in electrolyte concentration. Thus if at an appropriate pH the surfaces are negatively charged,  $\text{AZP}$  is positive i.e. zeta potential shifts towards zero and does not decrease further to the negative scale as manifest on rutile surface.

Discussion of the electrokinetic phenomenon by previous authors at rutile-water interface seems inadequate and cannot completely explain the results obtained in the present study. Present worker came across no reference where the authors had taken into consideration the peculiar nature of rutile surface arising out of strong electrical field due to  $\text{Ti}^{4+}$  ions in explaining their electrokinetic results. Furthermore the old concept of attraction between ions and oppositely charged surface particularly the simplistic model regarding the role of valency of counterions (Schulze and Hardy rule) in explaining the electrokinetic phenomenon in general seems to be grossly inadequate when applied to rutile-water interface e.g. this does not explain specific adsorption of

negatively charged ions on negatively charged rutile. Based on the present results and work done by other authors on rutile, a model of shear plane at rutile-water-interface has been suggested.

Before discussing the results, a detailed model of the rutile interface is being presented.

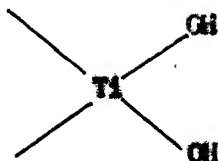
**5.2.1 Rutile Structure :** Rutile has tetragonal structure with titanium ions surrounded by six oxygen ion in the form of an octahedron<sup>44</sup>). Two of the Ti-O bond distances are 2.01 Å° and other four 1.92 Å°<sup>45</sup>). In the rutile unit cell the titanium and oxygen ions have been assigned diameters of 1.32 Å° and 2.58 Å° respectively<sup>46</sup>). The (100) and (110) planes are considered most important. These are the only planes along which the cleavage is distinct<sup>46</sup>).

**5.2.2. Adsorption at rutile surface :** At a freshly fractured surface, co-ordination of some ions must be incomplete. The nature of the solid-liquid interface produced by fracture of rutile and then immersion in water will depend primarily upon the kinds of chemical bonds broken in the fracture process. In rutile, the fracture involves rupture of primary ionic or covalent bonds and a polar or hydrophilic surface results<sup>47</sup>). The properties of such solid-liquid interface can be considered in terms of the reactions of water dipoles with broken bonds along the fractured surface. The electrical double layer at these interfaces is a manifestation of the ability of the water molecules to be polarized and to dissociate under the influence of electrostatic field of solid lattice. On a hydrophilic surface, the particle charge is created by preferential adsorption of certain specific ions on the particle surface. Such ions are called peptizing ions for the particle<sup>48</sup>), since they create the stabilising or peptizing charge. The adsorbed peptizing ions constitute the inner coating of

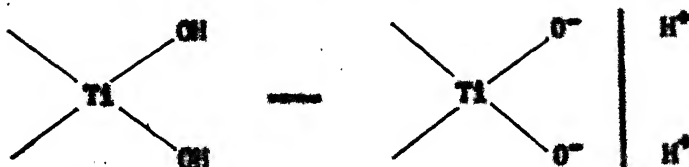
the electrical double layer. An equivalent amount of counterions is accumulated near the charged surface constituting the outer coatings of the double layer. Water itself sometimes acts as peptizing electrolyte as we shall see in case of rutile. Particles in solution will acquire a charge because of their surface and adsorption of ions. Because most of the ionization groups are weak electrolytes and because the binding energies for adsorption are of the order of the thermal energies, the surface charge situation must be described as an equilibrium between ions bound to the surface and ions in solution<sup>49</sup>). If the particles are brought to motion under the effect of some external force, it is expected they will carry with them an adsorbed layer of liquid. The zeta potential of particles is generally taken for the potential value on the boundary between the free liquid and the liquid adhering to the surface of a particle. However it should be noted that this potential is not solely determined by preferential ion adsorption but is largely characteristic of the solid itself<sup>50</sup>). Factors such as valency, size, density etc. of the atoms in the solid lattice will influence the distribution of ions in the interfacial region of solid and liquid.

It has been observed in the present study and previous studies mentioned in Chapter I that rutile attains a negative potential in neutral water. Increase in hydrogen ion concentration makes potential less negative while increase in hydroxyl ion concentration makes it more negative. The double layer should therefore be supposed to arise from adsorption of  $H^+$  and  $OH^-$  by the solid; in water alone an excess adsorption of the latter would account for the negative surface. So it is necessary to consider the wetted rutile surface as being composed of amphoteric units of the type





The reaction in neutral or slightly acid solution being



According to Buchanan et al<sup>52)</sup> the highly mobile hydrogen ions reside in the outer part of the double layer and the surface is left with a negative charge. The existence of hydroxyl groups on the surface of the insoluble oxides has been demonstrated<sup>52,53)</sup> by the determination of the water content of powder by studies of wetting heat and more directly by the measurement of infrared adsorption spectra. Young<sup>55)</sup> has reported that insoluble oxides retain a small amount of water even after it has been evacuated at a high temperature. Tetsuo Morimoto et al<sup>26)</sup> suggested that when the rutile surface is equilibrated with water, the surface hydroxyl groups will be formed by surface hydration. Further, these hydroxyl groups may be dissociated in two ways



According to them if the dissociation of surface hydroxyl groups occurs along equation (a) it will make the surface positive and basic at the same time and if dissociation proceeds as in equation (b) the surface will become negative and acidic. Buchanan et al<sup>56)</sup> have shown that ions can be physically adsorbed by a surface already possessing a charge of the same sign, the extent of adsorption

being independent of reasonable changes in the magnitude of the charge of the surface.

Considerable work has been done regarding the physical state of rutile when contacted with liquid water. Yates<sup>57)</sup>, Lewis and Parfitt<sup>58)</sup> investigated rutile surface by heats of adsorption studies and Wade et al<sup>59)</sup> by heat of immersion studies. Mays and Brady<sup>60)</sup> reported some results on proton magnetic resonance in water adsorbed on rutile. They found that in highly evacuated samples there is still some residual water present in measurable quantity. They further reported that under low coverage conditions all the water molecules are held to rutile surface by chemical forces of sufficient strength to prevent formation of ice clusters at 77°K.

In nutshell, these studies confirm the presence of hydroxyl groups on the rutile surface which may have been even outgassed at 450°C<sup>57,58)</sup>. For all practical purposes samples used in present study should have hydroxylated layers on them. Besides, these studies also confirmed the strong chemisorption of water and showed intermolecular hydrogen bonding to be characteristic of molecular water adsorbed on to the surface hydroxyl groups.

**5.2.3 Rutile - water interface :** Before discussing the interface it is useful to have a look at the structure of water. The most popular model proposed by Frank and Wen<sup>61)</sup> postulates that the formation of hydrogen bonds in water is predominantly a co-operative phenomenon so that in most cases when one bond forms several form, and when one bond breaks, then typically a whole cluster dissolves. This gives a picture of flickering clusters of various sizes and shapes jumping to attention and then relaxing at ease; half life of this structure may be between  $10^{-10}$  and  $10^{-11}$  sec.. The shape of these clusters has been

variously proposed : four co-ordinated structures of Nemethy and Scheraga<sup>62)</sup> lacking long range regularity, polyhedral cages of Pauling<sup>63)</sup> and Frank and Quist<sup>64)</sup> etc.. Regarding the rutile-water interface, one should expect strong chemisorption of water near the rutile surface in the form of hydroxyl groups. Beyond this hydroxyl layer there should be an oriented layer of water molecules hydrogen bonded to the surface hydroxyl groups. Putting the same thing in other words, the liquid phase and solid phase are stably bridged through the medium of oriented hydroxyl groups which in turn impose order on the surrounding liquid by intermolecular hydrogen bonding. The ordering process is further promoted by polarization effect of strong crystal field due to highly charged Titanium ions ( $Ti^{4+}$ ). This order becomes progressively weaker as we approach the bulk water through a transition region finally ending up in differently organized liquid. The transition zone corresponds to a region of greatest disorganization of the liquid medium because of the opposing ordering effects on water molecules of the surface and of the hydrogen bonding co-ordination of flickering clusters<sup>37)</sup>. This transition region will be characterized by less order than is exhibited by the bulk liquid phase and the ordered surface water molecules. The location of the shear plane at which the zeta potential is measured, is closely related to this region of high structural disorder as suggested by Berube and De Bruyn<sup>37)</sup>. This region is a kind of vacuum region where the forces opposing the relative motion of solid surface and bulk liquid are least. Hence the shear plane may exist in this region. It is in this region that ions will enter and leave the surface phase. Berube and De Bruyn assumed that the degree of dissociation of surface water into hydrogen and hydroxyl ions is significantly higher than that of normal and differently structured water. In support of this postulate, they cite the strong chemisorption of water at the surface which might be viewed as dissociation process.

The double layer is probably formed in the region of ordered water molecules because of presence of the dissociation products of water that is hydrogen and hydroxyl ions. The schematic picture of the proposed model is shown in Figure 4. Region 'BH' corresponds to the region of ordered water molecules in this region double layer lines.

Since in the present study electrolytes were used to study the zeta potential of rutile, it is necessary to study the effect on rutile-water interface due to the addition of these electrolytes. The effect can be studied under three different types of interactions :

**5.2.4 Electrolyte-water interaction :** As the internal field of water is controlled by electrostatic field of dipoles, the introduction of charged ions by the addition of electrolyte to water will obviously modify the field considerably. In case of ions of large sizes and small charges it is expected they will induce lot of disorder in the water and their tendency in general can be termed as structure breaking<sup>65,66</sup>). On the other hand, small ions with relatively large charge can orient the water molecules to such positions so as to favour mutual hydrogen bonding. These ions in general can be termed as structure promoting ions. Vaslow<sup>67</sup>) suggested that structure forming ions can fit into holes in cluster, distorting but not disrupting the structure, whereas the larger ions which are structure breaking apparently do not fit into holes. Frank and Evans<sup>68</sup>) have approximately calculated the so called "Structure breaking entropy" of water electrolyte solutions. Their calculations on alkali and halide ions show that the structure breaking entropy corresponding to the degree of disorder is greatest for the largest ions.

**5.2.5 Electrolyte shear plane region interaction :** It is expected that water will have a tendency to expel the structure breaking ions from the solution. In the rutile-water interface there is as mentioned earlier a region of high structural

order. The structure breaking ions should find a comfortable place to stay in this region of high disorder or in other words the concentration of structure breaking ions in this region should be higher than structure promoting ions.

**2.6 Ion-double layer region interaction :** The concentration of ions in the double layer region will depend primarily upon the affinity of double layer for such ions and secondarily upon the concentration of these ions in the region of maximum disorder, for the simple reason that ions from bulk water have to diffuse through this region to reach the double layer region. Scrube and De Bruyn have from thermodynamic considerations shown that the region of double layer will favour inorganic ions with strong hydration tendencies. So even though an ion may be structure breaker and its concentration higher in region of maximum disorder, yet it may not be favoured by the double layer region because of its relatively low hydration tendencies. In addition to above factors some specific ions may also get adsorbed in the region of double layer. Needless to say that number of such ions that can be accommodated in the interfacial region will be limited for the simple geometrical reasons.

Before we submit the tentative explanations of the experimental curves, let us have a look at the sizes, hydration tendencies and specific adsorbability of the ions used in the present work. Following<sup>70)</sup> table gives the valency and ionic sizes of various ions.

<u>Ion</u>	<u>Valency</u>	<u>Ionic Radius (Å)</u>
Cl	-1	1.81
Na	+1	0.97

K	+1	1.33
Ba	+2	1.34
Al	+3	0.51
Zr	+4	0.79

About the hydration number of various ions there is utter chaos in the literature as one can see in one of the latest review papers<sup>71)</sup> on the subject. The number assigned to any ion depends upon the method employed and the value of hydration number assigned to the reference ion. Following table gives the solvation number of various ions in water. The method employed was adiabatic compressibility

<u>Ion</u>	<u>Solvation number<sup>72)</sup></u>	<u>Solvation Number<sup>73)</sup></u>
Na <sup>+</sup>	3	6-7
K <sup>+</sup>	2	6-7
Ba <sup>++</sup>	8	16
Al <sup>+++</sup>	-	31
Cl <sup>-</sup>	3	1
NO <sub>3</sub> <sup>-</sup>	1	-

Specific adsorbability of ion depends upon its size, charge, sign of charge, and hydration<sup>74)</sup>. Bockris et al<sup>74)</sup> concluded for halide ions that increase in the ion size increases the adsorption on negatively charged mercury surface. Further they found cations tend to adsorb slightly less than anions. For rutile Berube and De Bruyn claim that ions which are heavily hydrated tend to be more specifically adsorbed than those which are not so hydrated.

Coming to experimental curves, a common feature to all the curves is noted viz. at low concentration of electrolyte all of them tend to increase the negative



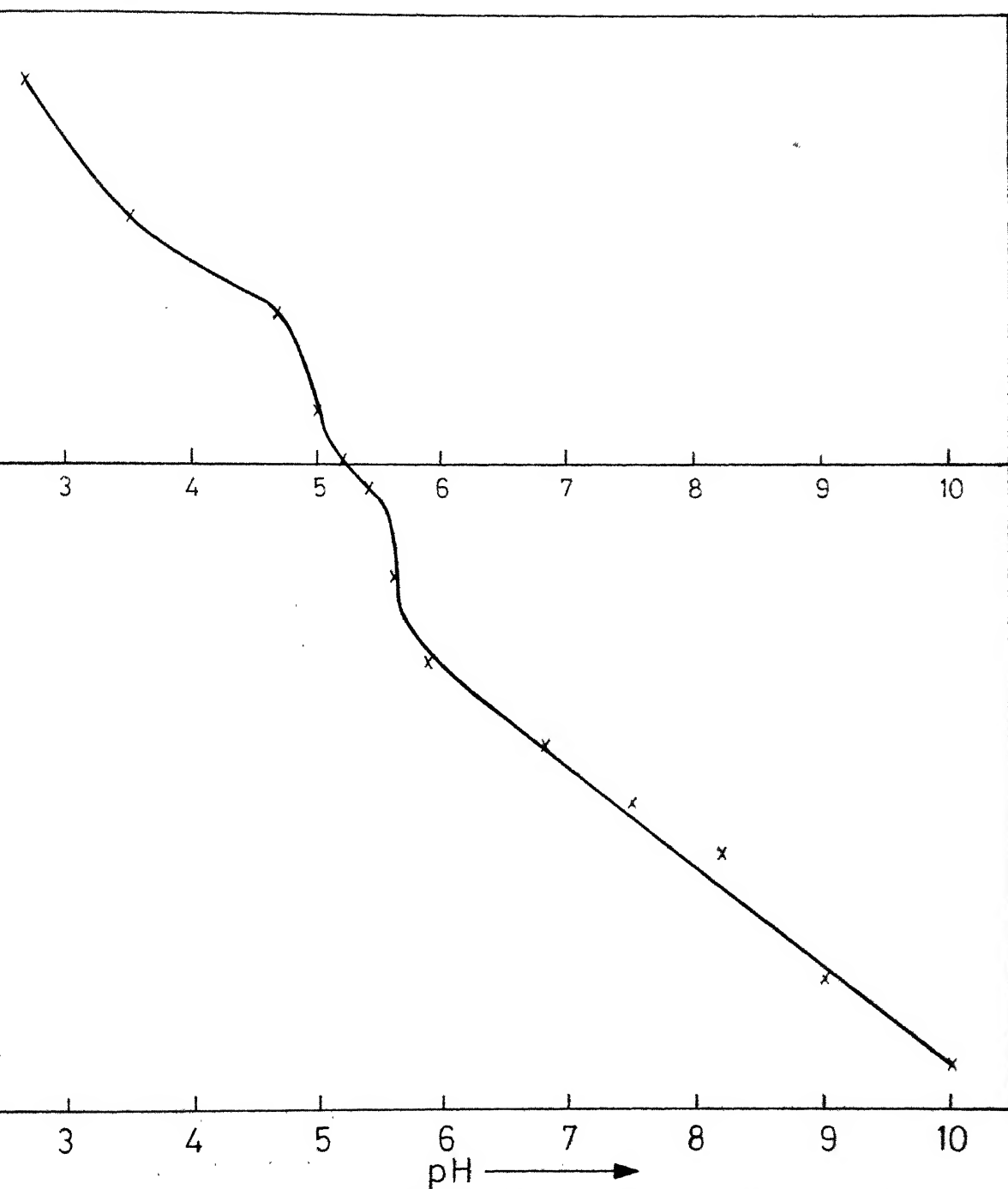
zeta potential of the system. This suggests that there is specific adsorption of negative ions at low concentration of electrolyte. A similar affinity for chloride ions has been reported for Zircon<sup>88)</sup> and Quartz<sup>91)</sup>. Affinity for negative ions seem to be stronger for rutile and Zircon where lattice cations are strongly electropositive. It may be recalled that  $\text{Cl}^-$  ions are potential determining for gold sols<sup>94)</sup>.

Results of Iribarni et al<sup>89)</sup> and Hermans<sup>90)</sup> show that the charge at the air-electrolyte (KCl) interface changes from positive to negative values as the concentration of electrolyte is increased. These results show that the chloride ions have a tendency to leave the aqueous solution and get adsorbed at the air-KCl solution interface. This escaping tendency may amount to proximity of the  $\text{Cl}^-$  ions near the rutile-water interface.

With this knowledge let us proceed to discuss the experimental curves :

**5.2.7 pH :** Figure (9) (Also see table 8, appendix 'D') depicts the change of zeta potential as pH is varied; while in Figure (10) (table 9, appendix 'D') effect of various electrolytes on zero point of charge (ZPC) is plotted.

Increase in pH means increase in the concentration of  $\text{OH}^-$  ions, hence more  $\text{OH}^-$  ions in shear plane region and double layer and therefore increase in negative potential. Likewise decrease in pH means increase in  $\text{H}^+$  ion concentration, hence less negative charge. In Figure 10 one can see that effect of KCl on ZPC is slight, whereas  $\text{BaCl}_2$  and  $\text{Zr}(\text{NO}_3)_4$  change it considerably. The effect of  $\text{Zr}^{4+}$  is greater than that of  $\text{Ba}^{++}$ . This shift in ZPC as explained by Benise and De Bruyn<sup>36)</sup> suggests the specific adsorption of positive ions in the interfacial region at these concentrations ( $10^{-4}$  M). For KCl there is no such evidence, but as Hunter and Wright<sup>76)</sup> mentioned, the shift in ZPC though a complete condition



9. VARIATION OF ZETA POTENTIAL OF RUTILE WITH pH.



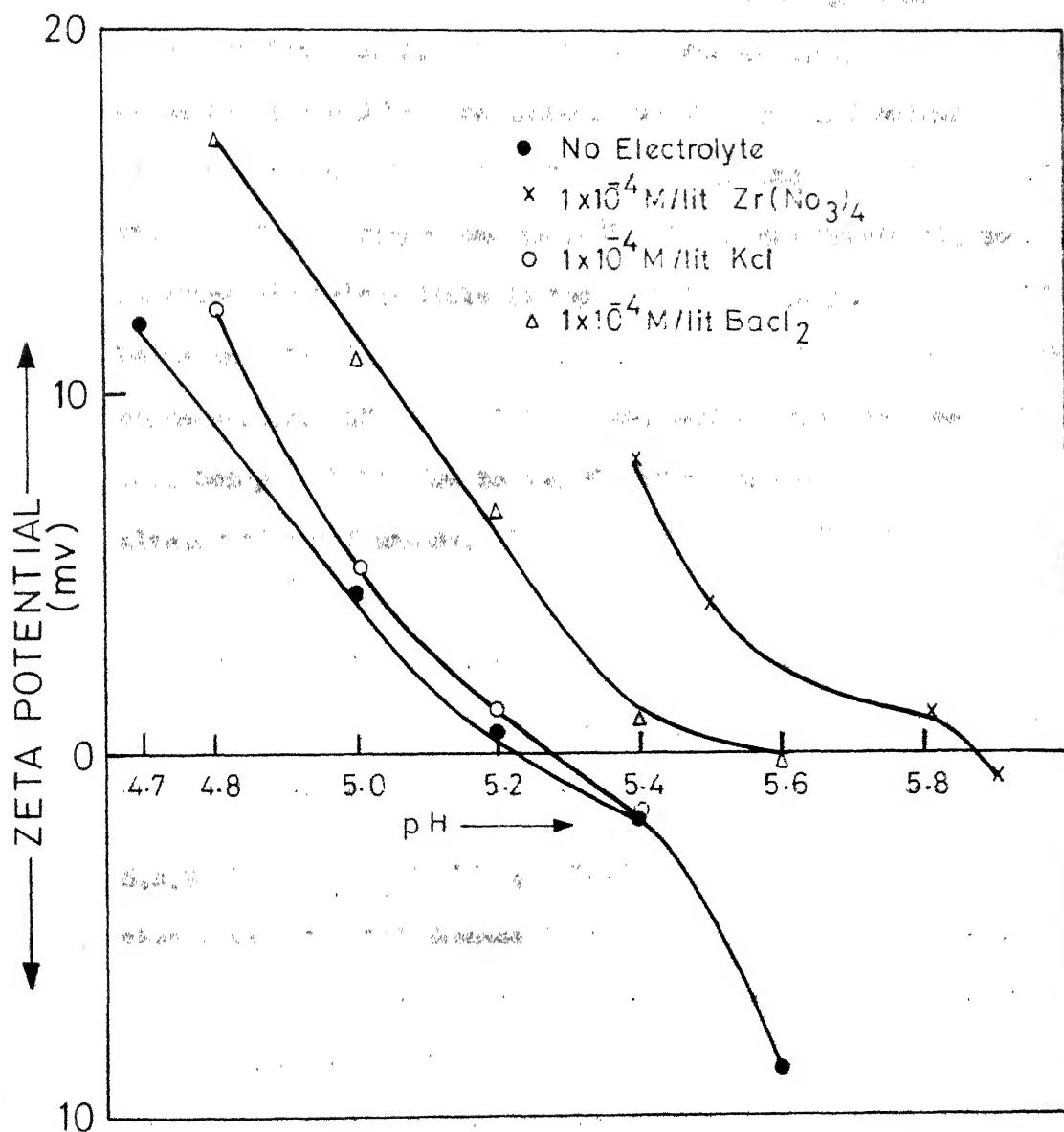


FIG.10 VARIATION OF ZPC OF RUTILE WITH pH IN DIFFERENT ELECTROLYTES.

of specific adsorption, is not a necessary condition. At concentration of  $10^{-4}$  M, there is evidence of specific adsorption of  $Ba^{++}$  and  $Zr^{++++}$  ions. But earlier we had noted that negative ions are getting adsorbed at low concentrations for all electrolytes. The possible explanation for this type of behavior could be that cations are repelled and anions attracted in low concentration of electrolyte because of strong positive electrical field in the interfacial region due to  $Ti^{4+}$ . It is not impossible to imagine strong positive electrical field in the interfacial region because this field also helps in orienting the water molecules as mentioned earlier. Only at higher concentrations of electrolyte do the cations move in the interfacial region. This being probably due to the shielding effect provided to the cations by the already adsorbed anions. A similar phenomenon has been observed by Gaudin and Fuerstman<sup>91)</sup> for quartz in NaCl. Increasing the concentration of NaCl till about  $10^{-4}$  equ./lit. increases the negative potential suggesting the specific adsorption of negative ions, but further increase decreases the negative potential suggesting the specific adsorption of positive ions.

**5.2.8 Potassium chloride :** Figure 5 (Also see Table 6, appendix 'D') shows that zeta potential changes to more negative values as concentration of KCl is increased. This is expected because  $Cl^{-}$  ions being large than  $K^{+}$  will have more structure breaking tendencies. Hence concentration of  $Cl^{-}$  ions in the shear plane region should be more compared to  $K^{+}$  ions. Due to this higher concentration, their concentration in the double layer region should be more and hence more negative potential is registered. The additional effect due to the strong electrical field around  $Ti^{4+}$  ions in lattice is also contributory to the phenomenon.

**5.2.9 Barium chloride :** Figure 6 (see also table 6, appendix 'D') shows that zeta potential increases to more negative values as concentration of  $BaCl_2$  is

increased. From the slope of the curve one can see that initially rate of increase in negative potential is more and then starts decreasing at high concentration of  $\text{BaCl}_2$ . Initially more  $\text{Cl}^-$  ions are getting adsorbed by the reasoning given in Section (5.2.7). Though the structure breaking tendency of  $\text{Ba}^{2+}$  (higher valency and low size) appears to be less than that of  $\text{Cl}^-$  ions (low valency and higher size), yet  $\text{Ba}^{2+}$  ions are more hydrated; so due to these opposing trends the potential should tend to stabilize as the concentration is increased beyond a stage of initial adsorption of  $\text{Cl}^-$  ions. This stabilisation is observed at higher concentration ( $10^{-4}$  M) in Figure 6 when the curve tends to flatten.

**5.2.10 Aluminium chloride :** The charge on  $\text{Al}^{3+}$  ions is more than that of chloride ions, its size is lesser and hence probably  $\text{Al}^{3+}$  ions are more structure-promoters than  $\text{Cl}^-$  ions.  $\text{Al}^{3+}$  ions are heavily hydrated than  $\text{Cl}^-$  ions and hence should be preferred in double layer region - of course after the initial specific adsorption of  $\text{Cl}^-$  ions. Hence initially negative potential will increase and then as concentration is increased the negative potential will decrease due to incorporation of  $\text{Al}^{3+}$  ions in the interfacial region as reflected in figure 11 (Table 10, appendix 'D').

**5.2.11 Zirconium nitrate :** Following the similar reasoning as above, in Figure 12 (Table 10 appendix 'D') one sees initial increase in negative potential due to specific adsorption of  $\text{NO}_3^-$  ions being followed by intense adsorption of  $\text{Zr}^{4+}$  ions giving a decrease in negative potential which finally becomes positive.  $\text{Zr}^{4+}$  ions though better structure promoters than  $\text{NO}_3^-$  (Low valency, high size) possess strong hydration tendencies and hence they will be preferred in double layer region. Beyond the concentration of  $8 \times 10^{-5}$  M of  $\text{Zr}(\text{NO}_3)_4$ , the zeta potential tends to become constant,  $\text{Zr}^{4+}$  being small ions with high charge will

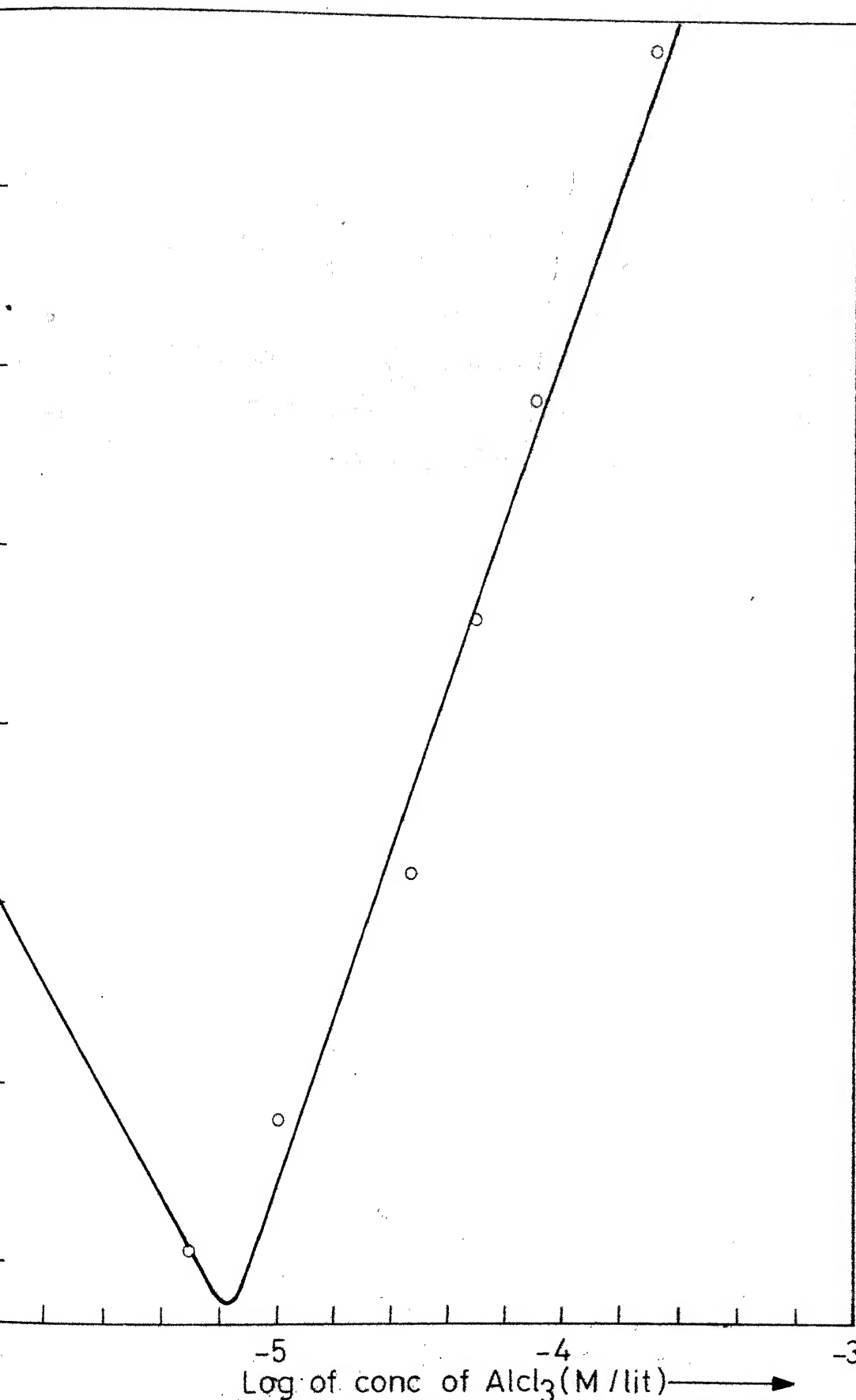


FIG.11 EFFECT OF ALUMINIUM CHLORIDE CONC. ON ZETA-POTENTIAL OF RUTILE.

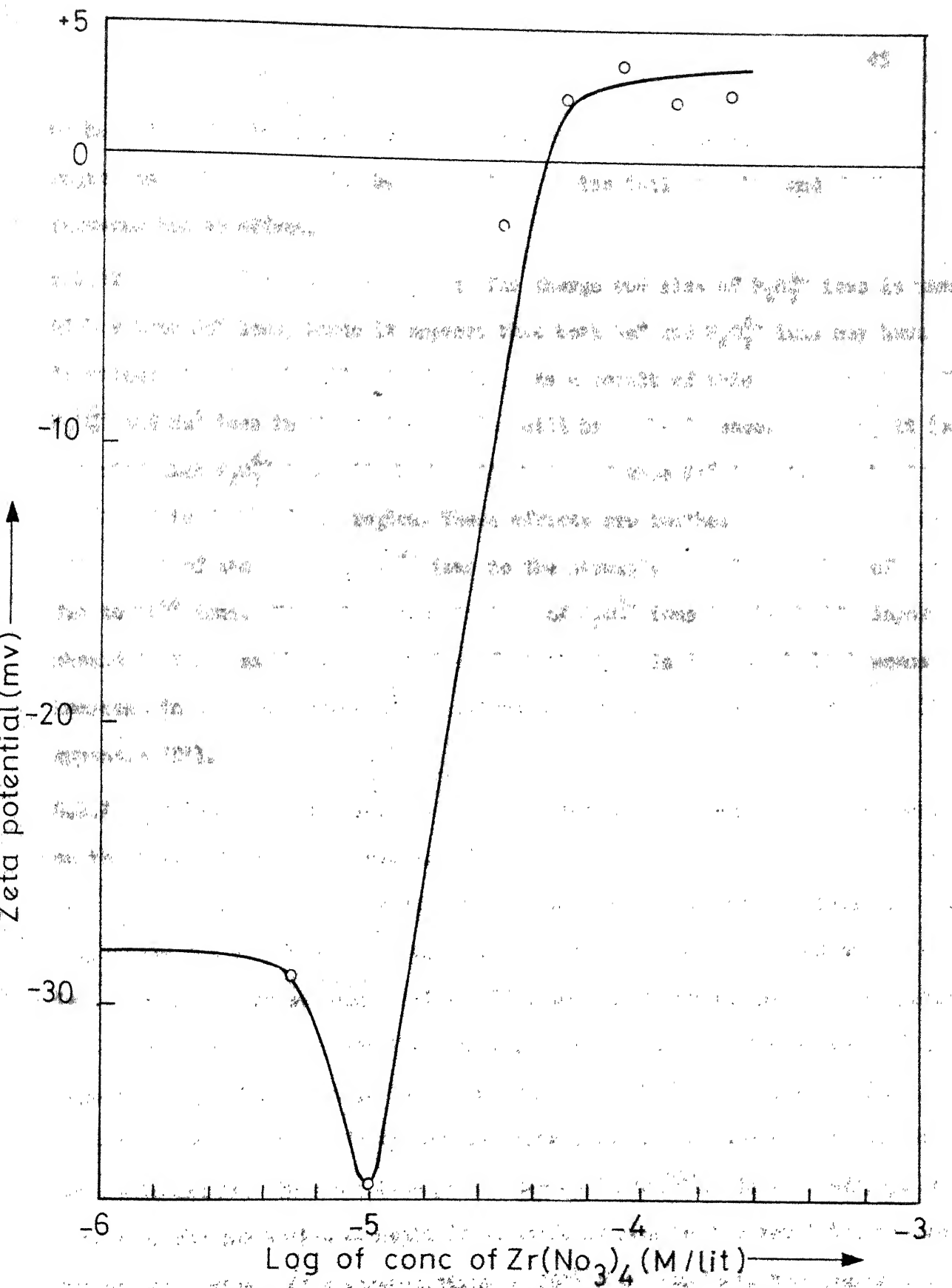


FIG.12. EFFECT OF ZIRCONIUM NITRATE CONC.ON ZETA POTENTIAL OF RUTILE.

be heavily hydrated. After certain concentration of  $\text{Zr}(\text{NO}_3)_4$ , the interfacial region is probably occupied by counterions to its full capacity and further increase has no effect.

**5.2.12 Tetra-Sodium pyrophosphate :** The charge and size of  $\text{P}_2\text{O}_7^{4-}$  ions is much higher than  $\text{Na}^+$  ions, hence it appears that both  $\text{Na}^+$  and  $\text{P}_2\text{O}_7^{4-}$  ions may have identical structure breaking tendencies. As a result of this concentration of  $\text{P}_2\text{O}_7^{4-}$  and  $\text{Na}^+$  ions in shear plane region will be probably same. However, it is expected that  $\text{P}_2\text{O}_7^{4-}$  ions will be heavily hydrated than  $\text{Na}^+$  ions hence should be preferred in double layer region. These effects are further compounded by the attraction of the negative  $\text{P}_2\text{O}_7^{4-}$  ions to the strongly positive surface of rutile due to  $\text{Ti}^{4+}$  ions. Hence the concentration of  $\text{P}_2\text{O}_7^{4-}$  ions in the double layer should increase as the concentration of electrolyte is increased which means increase in negative potential as reflected in Figure (13) (see also table 13, appendix 'D').

**5.2.13 Sodium Oleate :** The results with Naol and non-ionic can not be explained on the basis of the above theory. Oleate ions being very large and hydrophobic will tend to adsorb on rutile surface more than any other ion. Oleate ions being negatively charged should increase negative potential as concentration of Naol is increased as can be seen in Figure 14 (Table 11 appendix 'D'). This figure also shows the effect of non-ionic Naol on the zeta potential (see table 12, appendix 'D'). Non-ionic in the concentration of  $10^{-6}$  M has little effect. At higher concentrations ( $10^{-4}$  M) however there will be co-adsorption of oleate and non-ionic chains. This has been postulated by Bansal<sup>75</sup>). This co-adsorption increases the adsorption of oleate ions, since it reduces the repulsion between two oleate chains. At a concentration of  $10^{-6}$  M of non-ionic the increase in adsorption of oleate ions as reported by Bansal is very less. Hence we should expect at low concentration of non-ionic lesser effect, and at higher concentrations considerable increase in negative potential (vide Figure 14).

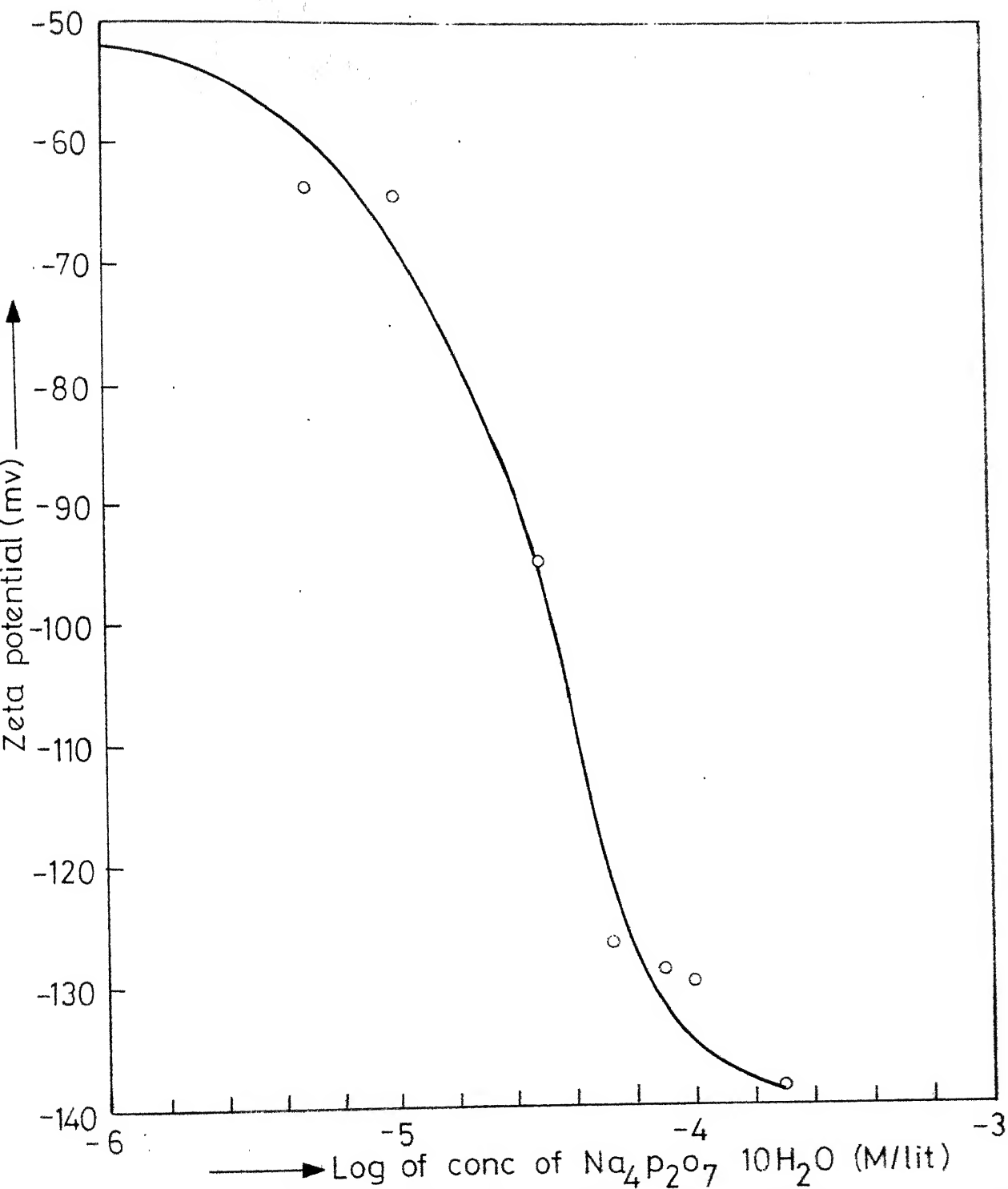


FIG. 13. EFFECT OF TETRA SODIUM PYROPHOSPHATE CONC. ON ZETA POTENTIAL OF RUTILE.

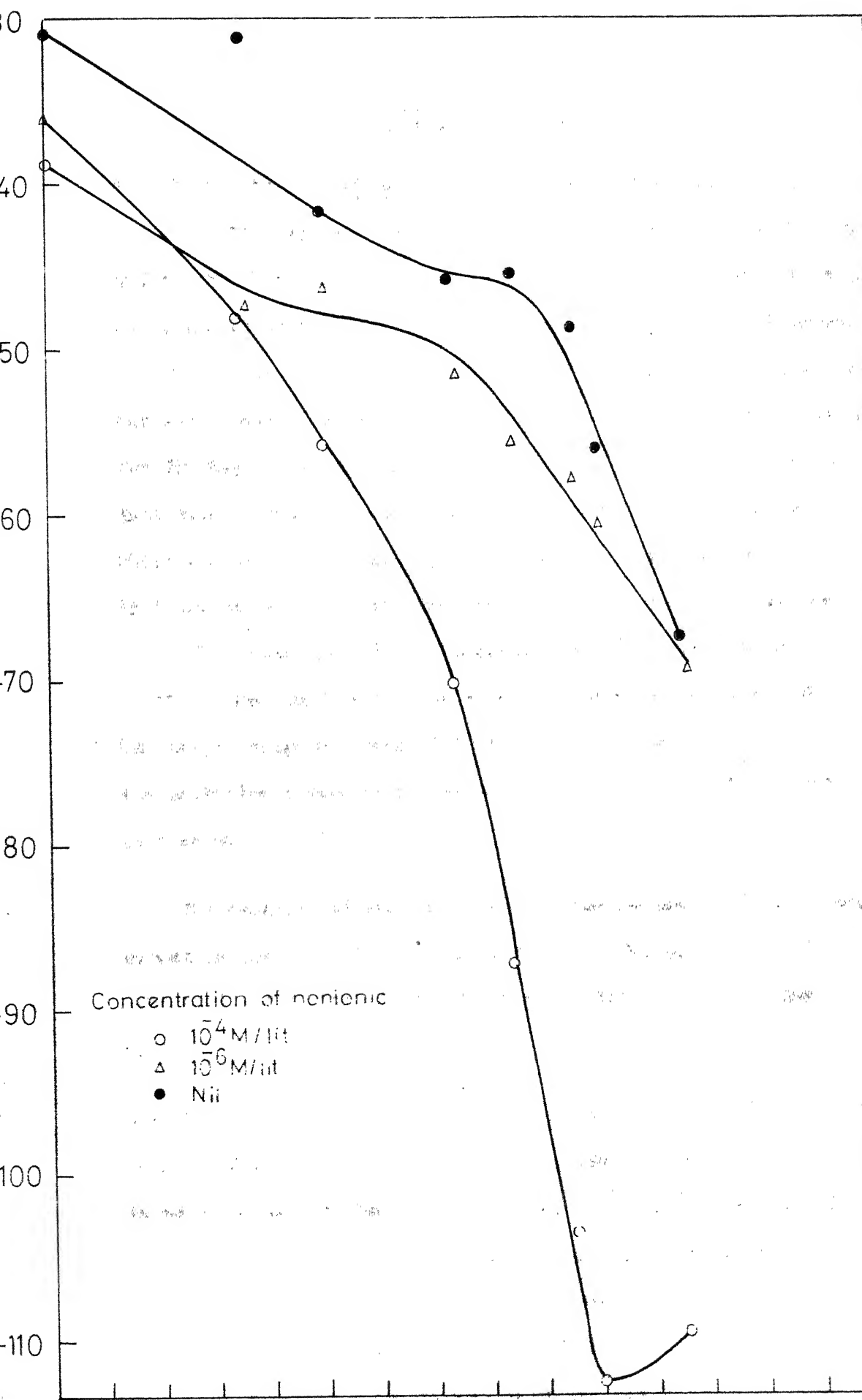


FIG. 14. EFFECT OF CONCENTRATION OF SODIUM OLEATE & NON-IONIC ON ZETA POTENTIAL OF RUTILE.



## CHAPTER 6 CONCLUSIONS

**6.1 Sedimentation potential :** The present work was carried out to study the comparison of zeta potential values obtained by sedimentation potential and electrophoretic mass transport analyser. The comparison is good in some cases and is at times way out different. This is due to inherent difficulties experienced in the measurement of 'SP'. The chances of errors are too many and experimental difficulties numerous than other methods. The method adopted for finding weight of material between electrodes appears to be more reliable than other method but needs more experience to handle besides being cumbersome. While comparing  $\zeta_{sp}$  with  $\zeta_{em}$ , it seems that mathematical equations regarding 'SP' are correct within experimental error. The equations can be applied with reasonable accuracy, if the concentration of electrolyte is very high and the particles are small enough so as to settle down slowly and give a stable potential but large enough as compared to the thickness of double layer. For better results the particles should be in low concentration in solution besides being as uniform in size as possible.

The geometry of particles in the size ranges considered, seems to have no effect on the comparison of  $\zeta_{sp}$  and  $\zeta_{em}$ . Though glass beads were perfectly spherical and rutile of all odd shapes, still comparison for rutile is as good as that for glass.

**6.2 Electrophoretic mobility of rutile :** The present work is an extension of Berube and De Bruyn's<sup>36,37</sup> work, in which they were interested in the double layer formation and not much concerned about the shear plane on rutile surface. The present work is mainly concerned about the electrokinetic phenomenon and hence the shear plane. In the current study, a probable location of shear plane has been suggested, which is at some distance beyond the solid surface in a region of greatest disorganisation of the liquid medium. This disorder arises

because of the opposing ordering effects on water molecules of the surface and hydrogen bonding co-ordination of the flickering clusters. The incorporation of various ions in the shear plane region and double layer region depends upon the specific adsorption of ions and interaction between ion and water molecules in the bulk. Behavior of the rutile surface in presence of various electrolyte solutions has been explained in terms of the properties of cations and anions viz. charge, size, hydration, compatibility with water structure, as well as valency and possible electrostatic interaction with the solid substrate.

Since adsorption studies were not carried out, it is difficult to give further justification to this model. Furthermore, anatase as the impurity in the rutile sample complicates the situation.

On the basis of the results obtained in this study, predictions regarding flotation behavior of rutile mineral in collector - modifier system (viz. test electrolyte solutions) may be ventured.

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Appendix ASIZING ANALYSIS OF RUTILE AND GLASS PARTICLESTable No. 1 : Sizing analysis of glass particles

Size in Microns ( $10^{-4}$ cm.)	Number of Particles	Percent of total
5.0	233	7.330
7.5	1275	40.100
10.0	508	16.000
12.5	544	17.100
15.0	320	10.050
17.5	194	6.100
20.0	63	1.980
22.5	30	0.930
25.0	10	0.314
27.5	3	0.096
<b>TOTAL</b>	<b>3180</b>	<b>100.000</b>

**Table No. 2 : Sizing analysis of rutile particles**

<b>Size in microns</b>	<b>Number of particles</b>	<b>Percent of the total</b>
2.50	151	11.840
3.75	197	17.800
5.00	206	18.600
6.25	202	18.280
7.50	161	14.520
8.75	95	8.582
10.00	49	4.423
11.25	42	3.792
12.50	48	1.623
13.75	6	0.540
<b>TOTAL</b>	<b>1107</b>	<b>100.00</b>

Appendix BX-RAY PATTERN RESULTSTable No. 3 : X-ray power pattern of rutile

Literature <sup>43)</sup>			Calculated	
$d, \text{\AA}^\circ$	$I/I_0$	hkl	$d, \text{\AA}^\circ$	$I/I_0$
3.245	100	(110)	3.26	100
2.489	41	(101)	2.49	43.8
2.188	22	(111)	2.19	23.5
2.054	9	(210)	2.09	11.8
1.687	50	(211)	1.68	50
1.624	16	(220)	1.64	17.6
1.48	8	(002)	1.455	8.5
1.36	16	(112)	1.37	18

Appendix CSEDIMENTATION POTENTIAL RESULTSTable No. 4 : Zeta potential of rutile in KCl and BaCl<sub>2</sub> by sedimentation Potential technique.Temperature = 27°C

Conc. of electrolyte (Mol./lit.)	KCl (pH = 6.5 ± 0.2)		BaCl <sub>2</sub> (pH = 6.65 ± 0.05)	
	R (ohms-cms.)	ZP (mV)	R (ohms-cms.)	ZP (mV)
0	$3.7 \times 10^5$	-22.98	$3.015 \times 10^5$	-23.12
$10^{-6}$	$3.2 \times 10^5$	-26.58	$3.012 \times 10^5$	-23.64
$5 \times 10^{-6}$	$2.45 \times 10^5$	-32.32	$2.16 \times 10^5$	-31.03
$10^{-5}$	$1.8 \times 10^5$	-37.47	$1.17 \times 10^5$	-44.76
$3 \times 10^{-5}$	$1.1 \times 10^5$	-55.99	$9.18 \times 10^4$	-43.36
$5 \times 10^{-5}$	$9.3 \times 10^4$	-56.76	$6.07 \times 10^4$	-48.31
$8 \times 10^{-5}$	$7.62 \times 10^4$	-46.18	$4.18 \times 10^4$	-50.11
$10^{-4}$	$5.8 \times 10^4$	-50.56	$3.5 \times 10^4$	-53.87
$2 \times 10^{-4}$	$3.0 \times 10^4$	--	$2.5 \times 10^4$	-58.66

**Table No. 5 : Zeta potential of glass beads in KCl and BaCl<sub>2</sub> by sedimentation potential technique.**

**Temperature = 27°C.**

Conc. of electrolyte (M/lit.)	KCl (pH = 6.85 ± 0.15)		BaCl <sub>2</sub> (pH = 6.9 ± 0.1)	
	R (ohm-cm.)	ZP (mV)	R (ohm-cm.)	ZP (mV).
0	$1.58 \times 10^5$	-27.89	$1.7 \times 10^5$	-27.52
$10^{-6}$	$1.04 \times 10^5$	-39.93	$1.19 \times 10^5$	-38.57
$5 \times 10^{-6}$	$1.02 \times 10^5$	-42.98	$1.06 \times 10^5$	-43.39
$10^{-5}$	$9.6 \times 10^4$	-30.48	$9.2 \times 10^4$	-45.39
$3 \times 10^{-5}$	$9.0 \times 10^4$	-25.36	$8.7 \times 10^4$	-48.37
$5 \times 10^{-5}$	$8.3 \times 10^4$	-17.91	$7.3 \times 10^4$	-45.71
$8 \times 10^{-5}$	$6.5 \times 10^4$	-9.63	$6.8 \times 10^4$	-24.54
$10^{-4}$	$5.8 \times 10^4$	+10.77	$6.4 \times 10^4$	-12.99
$2 \times 10^{-4}$	$5.2 \times 10^4$	+15.97	$5.9 \times 10^4$	-10.57

APPENDIX DELECTROKINETIC DATA OF RUTILE AND GLASS PARTICLES \*Table No. 6 : Zeta potential of rutile in KCl and BaCl<sub>2</sub> by 'EMTA'.

Conc. of electrolyte (M/lit.)	KCl (pH = 6.68 ± 0.15)		BaCl <sub>2</sub> (pH = 6.75 ± 0.15)	
	R (ohm-cm.)	ZP (mV)	R (ohm-cm.)	ZP (mV)
0	$4.05 \times 10^5$	-24.39	$2.15 \times 10^5$	-24.46
$10^{-6}$	$3.05 \times 10^5$	-26.02	$1.44 \times 10^5$	-28.42
$5 \times 10^{-6}$	----	---	$9.3 \times 10^4$	-34.67
$10^{-5}$	$1.58 \times 10^5$	-27.23	$8.0 \times 10^4$	-34.74
$3 \times 10^{-5}$	$1.03 \times 10^5$	-37.36	$5.6 \times 10^4$	-44.44
$5 \times 10^{-5}$	$7.5 \times 10^4$	-35.12	$4.0 \times 10^4$	-51.13
$8 \times 10^{-5}$	$5.6 \times 10^4$	-37.04	$3.07 \times 10^4$	-54.41
$10^{-4}$	$4.7 \times 10^4$	-44.40	---	---
$2 \times 10^{-4}$	$2.75 \times 10^4$	-55.73	$1.7 \times 10^4$	-59.51

\* Temperature was maintained at 27°C for all the studies carried out by 'EMTA'.

**Table No. 7 : Zeta potential of glass spheres in KCl and BaCl<sub>2</sub> by 'EMTA'.**

Conc. of electrolyte (M/lit.)	KCl (pH = 6.7 ± 0.1)		BaCl <sub>2</sub> (pH = 6.95 ± 0.1)	
	R (ohm-cm.)	ZP (mV)	R (ohm-cm.)	ZP (mV)
0	$1.01 \times 10^5$	-27.72	$9.8 \times 10^4$	-27.59
$10^{-6}$	$5.1 \times 10^4$	-35.33	$5.3 \times 10^4$	-30.15
$5 \times 10^{-6}$	$4.35 \times 10^4$	-31.62	$4.3 \times 10^4$	-35.42
$10^{-5}$	$4.05 \times 10^4$	-28.76	$3.4 \times 10^4$	-38.48
$5 \times 10^{-5}$	$2.95 \times 10^4$	-14.07	$3.05 \times 10^4$	-41.8
$5 \times 10^{-5}$	$2.5 \times 10^4$	-14.22	$2.18 \times 10^4$	-22.32
$8 \times 10^{-5}$	$2.23 \times 10^4$	-13.44	$1.81 \times 10^4$	- 9.958
$10^{-4}$	$1.91 \times 10^4$	-10.07	$1.6 \times 10^4$	- 9.16
$2 \times 10^{-4}$	$1.34 \times 10^4$	+ 5.62	$1.1 \times 10^4$	- 2.28

**Table No. 8 : Zeta potential of rutile as a variable of pH by 'EMTA'.**

pH	Zeta potential (mV)
2.7	+ 29.56
3.5	+ 19.31
4.7	+ 11.64
5.0	+ 4.19
5.2	+ 0.39
5.4	- 1.89
5.6	- 8.65
5.9	- 15.12
6.8	- 24.32
7.5	- 26.32
8.2	- 30.15
9.0	- 39.58
10.0	- 46.51



**Table No. 9 : Zeta potential of rutile as a variable of pH in different electrolytes at constant concentration by 'EMTA'.**

pH	Zeta potential (mV)		
	KCl = $10^{-4}$ M	BaCl <sub>2</sub> = $10^{-4}$ M	Zr(NO <sub>3</sub> ) <sub>4</sub> = $10^{-4}$
4.8	+ 12.15	+ 17.15	--
5.0	+ 5.12	+ 11.25	--
5.2	+ 1.15	+ 6.89	--
5.4	- 1.70	+ 1.23	+ 8.05
5.6	--	0.00	+ 4.03
5.8	--	--	+ 1.01
5.9	--	--	- 0.71

Table No. 10 : Zeta potential of rutile in  $\text{AlCl}_3$  and  $\text{Zr}(\text{NO}_3)_4$  by 'EMTA'.

Conc. of electrolyte (M/lit.)	Zeta potential (mV)	
	$\text{AlCl}_3$ (pH = $6.5 \pm 0.1^*$ )	$\text{Zr}(\text{NO}_3)_4$ (pH = $6.6 \pm 0.1^*$ )
0	- 24.95	- 24.75
$10^{-6}$	- 28.02	- 48.69
$5 \times 10^{-6}$	- 28.86	- 69.28
$10^{-5}$	- 36.62	- 62.00
$5 \times 10^{-5}$	- 2.16	- 48.12
$5 \times 10^{-5}$	+ 2.45	- 33.94
$8 \times 10^{-5}$	+ 3.71	- 21.57
$10^{-4}$	+ 2.39	- 1.64
$2 \times 10^{-4}$	+ 2.75	--

\* pH adjusted.

**Table No. 11 : Zeta potential of rutile in  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  and Naol by 'EMPA'.**

Concentration of electrolyte (M/lit.)	Zeta potential (mV)	
	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (pH=7.0±0.1*)	Naol (pH=6.9±0.1)
0	- 24.65	- 24.82
$10^{-6}$	- 51.77	- 38.73
$5 \times 10^{-6}$	- 63.31	- 31.15
$10^{-5}$	- 63.49	- 41.73
$3 \times 10^{-5}$	- 94.63	- 48.63
$5 \times 10^{-5}$	-126.81	- 48.35
$8 \times 10^{-5}$	-128.50	- 48.82
$10^{-4}$	-129.70	- 56.10
$2 \times 10^{-4}$	-138.39	- 67.47

\* pH value adjusted.

**Table No. 12 : Zeta potential of rutile in non-ionic-Naol by 'EMTA'.**

Concentration of Naol. (M/lit.)	Zeta potential	
	Conc. of non-ionic= $10^{-6}$ M (pH = $6.7 \pm 0.20$ )	Conc. of non-ionic= $10^{-4}$ M (pH = $6.65 \pm 0.15$ )
0	- 24.52 *	- 24.42 *
$10^{-6}$	- 38.77	- 36.09
$5 \times 10^{-6}$	- 47.37	- 47.84
$10^{-5}$	- 46.24	- 55.61
$3 \times 10^{-5}$	- 51.47	- 70.21
$5 \times 10^{-5}$	- 55.57	- 87.31
$8 \times 10^{-5}$	- 57.75	-103.45
$10^{-4}$	- 60.42	-112.56
$2 \times 10^{-4}$	- 69.05	-109.58

\* Concentration of non-ionic zero.

APPENDIX ERATIO OF ZETA POTENTIALS DETERMINED BY 'SP' AND 'EMTA'  
TECHNIQUESTable No. 13 : Ratio of zeta potentials (R) of rutile calculated from  
electrophoretic mobility and sedimentation potential  
in KCl and BaCl<sub>2</sub>.

Concentration of electrolyte (M/lit.)	R = $\zeta_{em}/\zeta_{sp}$	
	Potassium chloride	Barium chloride
0	1.06	1.06
10 <sup>-6</sup>	0.98	1.20
5 × 10 <sup>-6</sup>	-	1.12
10 <sup>-5</sup>	0.74	0.78
3 × 10 <sup>-5</sup>	0.68	1.02
5 × 10 <sup>-5</sup>	0.62	1.05
8 × 10 <sup>-5</sup>	0.81	1.08
10 <sup>-4</sup>	0.88	-
2 × 10 <sup>-4</sup>	-	1.01

**Table No.14 : Ratio of zeta potentials of glass beads calculated from electrophoretic mobility and sedimentation potential in KCl and BaCl<sub>2</sub>.**

Concentration of electrolyte (M/lit.)	$R = \zeta_{em}/\zeta_{sp}$	
	Potassium chloride	Barium chloride
0	0.99	1.00
$10^{-6}$	0.88	0.78
$5 \times 10^{-6}$	0.74	0.82
$10^{-5}$	0.94	0.85
$3 \times 10^{-5}$	0.55	0.86
$5 \times 10^{-5}$	0.79	0.49
$8 \times 10^{-5}$	0.73	0.40
$10^{-4}$	- 0.94	0.71
$2 \times 10^{-4}$	0.36	0.22

APPENDIX FVALUES OF FUNCTION ' $\kappa a$ ' FOR RUTILE AND GLASS IN KCl AND BaCl<sub>2</sub>.

$$a_{\text{rutile}} = 6.02 \times 10^{-4} \text{ cm.}, a_{\text{glass}} = 10.39 \times 10^{-4} \text{ cm.}$$

$$\kappa^2 = 8.742 \times 10^{-7} \sum Z_i^2 n_i$$

Table No. 15 : Value of function ' $\kappa a$ ' in KCl.

$$n_1 = n^+ = n^- = I_D \times C \times 6.02 \times 10^{20} \text{ ions/cm.}^3$$

$$\sum Z_i^2 n_i (\text{for KCl}) = I_D \times C \times 6.02 \times 10^{20} \times 2.$$

(where  $I_D$  = Degree of ionization, C = Concentration in M/lit.)

C	$I_D^{(83)}$	$\kappa^2$ (cm. <sup>-2</sup> )	$\kappa a_{\text{rutile}}$	$\kappa a_{\text{glass}}$
$10^{-6}$	*	$105.95 \times 10^7$	19.4	33.6
$5 \times 10^{-6}$	*	$529.76 \times 10^7$	43.6	75.5
$10^{-5}$	*	$10.59 \times 10^9$	71.4	112.4
$5 \times 10^{-5}$	*	$31.78 \times 10^9$	114.0	185.0
$5 \times 10^{-5}$	99.5	$52.71 \times 10^9$	138.0	238.0
$8 \times 10^{-5}$	99.4†	$84.25 \times 10^9$	175.0	302.0
$10^{-4}$	99.3	$105.21 \times 10^9$	194.0	336.0
$2 \times 10^{-4}$	99.0	$209.78 \times 10^9$	274.0	472.0

\* Values not available in literature hence assumed 100 percent dissociation.

† Value extrapolated by plotting degree of ionization with log C.

Table No. 16 : Values of function ' $\kappa a$ ' in  $\text{BaCl}_2$ .

$$n_1 = n^\infty = 2n^0 = 2 \times 6.02 \times 10^{20} I_D \times C.$$

$$\text{I } Z_1^2 n_1 = 6 \times 12.04 \times 10^{20} I_D \times C.$$

C	$I_D^{(63)}$	$n^2$	$\kappa a_{\text{rutile}}$	$\kappa a_{\text{glass}}$
$10^{-6}$	98.8	$31.4 \times 10^8$	33.7	58.0
$5 \times 10^{-6}$	97.9	$15.56 \times 10^9$	75.0	129.5
$10^{-5}$	97.3	$30.92 \times 10^9$	105.0	182.0
$3 \times 10^{-5}$	95.9	$91.54 \times 10^9$	182.0	314.0
$5 \times 10^{-5}$	95.3	$143.8 \times 10^9$	228.0	392.0
$8 \times 10^{-5}$	94.0 <sup>†</sup>	$239.03 \times 10^9$	294.0	510.0
$10^{-4}$	93.9	$2.98 \times 10^{11}$	329.0	568.0
$2 \times 10^{-4}$	92.3	$5.88 \times 10^{11}$	451.0	802.0

† See footnote table no. 15.



APPENDIX GSEDIMENTATION POTENTIAL AND ELECTROPHORETIC MOBILITY CALCULATIONS.G.1 Employing Quist and Washburn's method :

Time taken by particles to fall in distilled water

= 2.38 sec./cm. (average of 70 readings).

Amount of solids flowing through stopcock 'S<sub>2</sub>' = 0.0227 gm./sec.

Distance between the two electrodes = 12.59 cms.

Time taken by particles to fall through a distance of 12.59 cms.

=  $2.38 \times 12.59 = 30$  sec.

Therefore weight of solids between the electrodes =  $30 \times 0.227 = 0.68$  gm.

Specific resistance =  $3.7 \times 10^5$  ohms.

For water : Viscosity ( $\eta$ ) =  $89 \times 10^{-4}$  poise.

Dielectric constant (D) = 80.

Density of solids (d) = 3.266,

Density of water at 27°C = 0.995 ( $d_0$ )

Area of the tube =  $10.64 \text{ cm.}^2$

Sedimentation potential developed (E) =  $- 47.97 \times 10^{-5}$  V.

From equation (1) (section 4.3.3)

$$\therefore E = \frac{E \times 4\pi A d \rho \times 10^{14}}{D R W (d - d_0) \eta} = - 37.92 \text{ mV.}$$

G.2 Employing method suggested by author :

Mass per unit volume =  $5 \times 10^{-3}$  gm./cm.<sup>3</sup>

Specific resistance =  $3.7 \times 10^5$  ohms.

Sedimentation potential developed =  $- 29 \times 10^{-5}$  V.

From equation (2) (section 4.2.2)

$$\zeta = \frac{1.0816 \times 10^8 E d}{R N (d - d_0)}$$

$$= - 22.98 \text{ mV.}$$

### G.3 Electrophoretic mobility method :

$$\text{Specific conductance } (\lambda) = \frac{1}{R} = \frac{1}{3.7 \times 10^5} = 2.7 \times 10^{-6} \text{ mho's.}$$

Current (i) =  $3 \times 10^{-4}$  amp.,  $t = 600$  seconds.

Concentration of particles (N) =  $0.05 \text{ gm./cm.}^3$ .

Change in weight ( $\Delta W$ ) =  $0.4348 \text{ gm.}$

Positive Test.  $\therefore i = - 3 \times 10^{-4} \text{ amp.}$

From equation (4) (section 4.4.2)

$$\zeta = \frac{15 \times 10^4 \times \Delta W \times \lambda \times d}{i \times t \times N \times (d - d_0)}$$

$$= - 24.39 \text{ mV.}$$

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'THE END'